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In re Japanese Application of

Toru TATSUMI

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for: "Method of Vapor Phase Growth of Metal Oxide Dielectric Film"

VERIFICATION OF TRANSLATION

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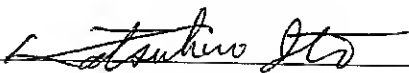
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[Title of the Invention] METHOD OF VAPOR PHASE GROWTH
OF METAL OXIDE DIELECTRIC FILM

[Claims]

5 [Claim 1]

A vapor phase growth method for carrying out film
formation of a metal oxide dielectric film with a
perovskite type crystal structure represented by ABO_3 on
a conductive material using organometal gases, comprising
10 steps of: carrying out initial nuclei formation of the
perovskite type crystal structure on the conductive
material using all of the organometal gases to be the raw
materials of the metal oxide dielectric film under first
film formation conditions, and carrying out film
15 formation of the perovskite type crystal structure
further on the initial nuclei under second film formation
conditions.

[Claim 2]

A vapor phase growth method for carrying out film
20 formation of a metal oxide dielectric film with a
perovskite type crystal structure represented by ABO_3 on
a conductive material using organometal gases, comprising
steps of: carrying out initial layer formation of the
perovskite type crystal structure on the conductive
25 material using all of the organometal gases to be the raw
materials of the metal oxide dielectric film under first

film formation conditions and carrying out film formation of the perovskite type crystal structure further on the initial layer under second film formation conditions.

[Claim 3]

5 A vapor phase growth method for carrying out film formation of a metal oxide dielectric film with a perovskite type crystal structure represented by ABO_3 on a conductive material using organometal gases, comprising steps of: carrying out initial nuclei formation of the
10 perovskite type crystal structure on the conductive material using only a part of the organometal gases to be the raw materials of the metal oxide dielectric film under first film formation conditions and carrying out film formation of the perovskite type crystal structure
15 further on the initial nuclei under second film formation conditions.

[Claim 4]

20 A vapor phase growth method for carrying out film formation of a metal oxide dielectric film according to any one of claims 1 to 3, wherein the second film formation conditions are so set as to carry out film formation using raw material gas supply in good self-controlling conditions, and the raw material of the A element is supplied in a higher quantity in the first
25 film formation conditions than that in the second film formation conditions.

[Claim 5]

A vapor phase growth method for carrying out film formation of a metal oxide dielectric film according to any one of claims 1 to 4, wherein the supply amount of Zr
5 in the B element, in the case where the B element includes both Zr and Ti, is decreased relatively to that of Ti in the first film formation conditions as compared with in the second film formation conditions.

[Claim 6]

10 A vapor phase growth method according to claim 3, wherein the first film formation conditions are so controlled as to supply no Zr raw material gas in film formation in the case Zr and other elements are contained as the B element.

15 [Claim 7]

A vapor phase growth method for carrying out film formation of a metal oxide dielectric film according to claim 1 or 3, wherein the film formation is carried out while controlling the crystal grain size by controlling
20 the duration time of the initial nuclei formation in the first film formation conditions.

[Claim 8]

A vapor phase growth method for carrying out film formation of a metal oxide dielectric film according to
25 any one of claims 1 to 7, wherein the total pressure of the raw material gases including the organometal gases at

the time of film formation is kept at 1×10^{-2} Torr or lower.

[Claim 9]

5 A vapor phase growth method for carrying out film formation of a metal oxide dielectric film according to claim 8, wherein the film formation temperature is kept at 450°C or lower.

[Claim 10]

10 A vapor phase growth method of a metal oxide dielectric film according to any one of claims 1 to 3, wherein the metal oxide dielectric film is a PZT film or a BST film.

[Claim 11]

15 A vapor phase growth method of a metal oxide dielectric film according to any one of claims 1 to 10, wherein the conductive material is a capacitor electrode comprising at least any one of metals and metal oxides of Pt, Ir, Ru, IrO₂, RuO₂, TiN, and WN.

[Claim 12]

20 A vapor phase growth method of a metal oxide dielectric film according to any one of claims 1 to 10, wherein the conductive material has a three-layered structure of Pt/TiN/Ti.

[Claim 13]

25 A vapor phase growth method of a metal oxide dielectric film according to any one of claims 1 to 10,

wherein the conductive material has a four-layered structure of Pt/TiN/Ti/W.

[Claim 14]

A method for fabricating a semiconductor device,
5 comprising: a step of forming a MOS-type transistor on a semiconductor substrate, a step of forming a first interlayer insulation film on the transistor, a step of forming electric conduction by opening a contact reaching the diffusion layer of the MOS-type transistor in the
10 first interlayer insulation film and burying a metal plug in the contact, a step of forming a capacitor lower part electrode layer on the whole surface of the first interlayer insulation film having the metal plug, a step of forming initial nuclei or an initial layer of a metal
15 oxide dielectric film having the perovskite type crystal structure on the whole surface of the capacitor lower part electrode layer using organometal gases under the first film formation conditions and further forming the metal oxide dielectric film having the perovskite type
20 crystal structure on the initial nuclei or the initial layer under the second film formation conditions, a step of forming a capacitor upper part electrode layer on the whole surface of the metal oxide dielectric film, and a step of patterning the capacitor lower part electrode
25 layer, the metal oxide dielectric film, and the capacitor upper part electrode layer to obtain a capacitor with a

three-layered laminated structure.

[Claim 15]

A method for fabricating a semiconductor device comprising: a step of forming a MOS-type transistor on a semiconductor substrate, a step of forming a first interlayer insulation film on the transistor, a step of forming electric conduction by opening a contact reaching the diffusion layer of the MOS-type transistor in the first interlayer insulation film and burying a metal plug in the contact, a step of forming a capacitor lower part electrode layer on the whole surface of the first interlayer insulation film having the metal plug, a step of forming a capacitor lower part electrode on the metal plug by patterning the capacitor lower part electrode layer, a step of forming initial nuclei or an initial layer of a metal oxide dielectric film having the perovskite type crystal structure on the whole surface of the patterned capacitor lower part electrode and the first interlayer insulation film layer using organometal gases under the first film formation conditions and further forming the metal oxide dielectric film having the perovskite type crystal structure on the initial nuclei or the initial layer under the second film formation conditions, a step of forming a capacitor upper part electrode layer on the whole surface of the metal oxide dielectric film, and a step of patterning the

capacitor upper part electrode layer to obtain a capacitor with a three-layered laminated structure of the capacitor lower part electrode, the metal oxide dielectric film, and the capacitor upper part electrode.

5 [Claim 16]

A method for fabricating a semiconductor device, comprising a step of forming a MOS-type transistor on a semiconductor substrate, a step of forming a first interlayer insulation film on the transistor, a step of forming electric conduction by opening a contact reaching the diffusion layer of the MOS-type transistor in the first interlayer insulation film and burying a metal plug in the contact, a step of forming an aluminum wiring on the first interlayer insulation film to electrically connecting the aluminum wire with the metal plug, a step of forming a second interlayer insulation film on the aluminum wiring, a step of forming electric conduction by opening a contact reaching the aluminum wiring in the second interlayer insulation film and burying a metal plug in the contact, a step of forming a capacitor lower part electrode layer on the whole surface of the second interlayer insulation film having the metal plug, a step of forming initial nuclei or an initial layer of a metal oxide dielectric film having the perovskite type crystal structure on the whole surface of the whole surface of the capacitor lower part electrode layer using

organometal gases under the first film formation conditions and further forming the metal oxide dielectric film having the perovskite type crystal structure on the initial nuclei or the initial layer under the second film formation conditions, a step of forming a capacitor upper part electrode layer on the whole surface of the metal oxide dielectric film, and a step of patterning the capacitor lower part electrode layer, the metal oxide dielectric film, and the capacitor upper part electrode layer to obtain a capacitor with a three-layered laminated structure.

[Claim 17]

A method for fabricating a semiconductor device according to claim 16, wherein aluminum wiring to be formed in the lower layer of the capacitor is made multilayered by repeating, at least one time before the capacitor lower part electrode layer is formed, a step of forming an aluminum wiring electrically conducting to the finally formed metal plug, a step of forming an interlayer insulation film on the aluminum wiring, and a step of forming electric conduction by opening a contact reaching the aluminum wiring in the interlayer insulation film and burying a metal plug in the contact.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a fabrication method of a semiconductor device having capacitor elements, more specifically, the present invention
5 relates to a fabrication method of a high-dielectric-constant film and a ferroelectric film, to be used for a capacitor and a gate of a semiconductor integrated circuit using raw materials of organometal gases.

[0002]

10 [Prior Art]

In recent years, ferroelectric memories using ferroelectric capacitors, dynamic random access memories (DRAMs) using high-dielectric-constant capacitors, and the likes have actively been investigated and developed.
15 These ferroelectric memories and DRAMs comprise selective transistors and store information using capacitors, as memory cells, connected to one diffusion layer of each selective transistor. The ferroelectric capacitors are provided with, as a capacitive insulating film, a
20 ferroelectric film such as $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (hereafter referred to as PZT) or the like and enabled to store non-volatile information by polarizing the ferroelectric film. Meanwhile, the high-dielectric-constant capacitors are provided with, as a capacitive insulating film, a high-
25 dielectric-constant thin film of $(\text{Ba}, \text{Sr})\text{TiO}_3$ (hereafter referred to as BST), so that the capacitors have high

capacitance and enable elements to be miniaturized in a fine structure.

[0003]

In the case of using such ceramic materials for
5 semiconductor elements, it is highly important to deposit
such ceramic materials in a thin film with excellent
crystallinity on a conductive film to be a lower
electrode. As the method for depositing a thin film,
there have conventionally been reported a sol-gel method,
10 a sputtering method, and a CVD method.

[0004]

The sol-gel method is a method in which organometal
materials dissolved in an organic solvent are applied to
a wafer having a lower electrode formed thereon, by a
15 spin coating, and crystallized by annealing in oxygen.
In the method, since crystallization takes place in a
solid phase, the temperature for the crystallization is
necessary to be very high and in the case of using PZT
for a metal oxide dielectric film, the crystallization
20 temperature required to acquire sufficient ferroelectric
properties is 600°C and in the case of BST, the
crystallization temperature required to acquire
sufficiently high dielectric properties is 650°C. A
crystal formed by the foregoing method has a defect that
25 the orientation of the crystal is uneven. Further, the
sol-gel method is difficult to be applied to a wafer with

a large diameter and furthermore, the method is inferior in coating of stepped surfaces and thus unsuitable for high integration of a device.

[0005]

5 The sputtering method is a method in which a film is formed on a wafer having electrodes thereon, by reactive sputtering of a ceramic sintered body to be formed into the film using Ar + O₂ plasma and then subjected to crystallization by annealing in oxygen. The
10 film can be made even by making the diameter of the target wide and a sufficiently high film formation speed can be obtained by increasing the power for plasma generation. However, in the sputtering method as well, the crystallization is required to be carried out at a
15 high temperature and in the case of using PZT for a metal oxide dielectric film, the crystallization temperature required to acquire sufficient ferroelectric properties is 600°C and in the case of BST, the crystallization temperature required to acquire sufficiently high
20 dielectric properties is 650°C. Further, in the sputtering method, since the composition of the film obtained is substantially determined by the composition of the target used, the target has to be replaced in order to change the composition and that is
25 disadvantageous from a viewpoint of production process.

[0006]

The CVD method is a method in which raw materials are transferred in gaseous state to a vacuum chamber to form a film. It is considered that the CVD method is excellent in uniform film formation on a wafer with a large diameter and in coating property on stepped surfaces and highly expected as a technique for mass production in the case of application to ULSI. The metals of constituent elements of a metal oxide dielectric film are Ba, Sr, Bi, Pb, Ti, Zr, Ta, La, and the likes and since proper hydrides and chlorides of these metals are very few, organometals are used for vapor phase growth. However, these organometals have low vapor pressures and are mostly solids or liquid at a room temperature and, therefore, a transferring method using a carrier gas is employed.

[0007]

Fig. 2 is a diagrammatic illustration illustrating the reaction gas supply method in the case of using a carrier gas. The apparatus is composed of a thermostatic tank 201, a bottle 202, organometal raw materials 203 made ready in the bottle, a supply pipe 204 for an inert carrier gas such as Ar, N₂, and the likes, a mass flow controller 210 for the carrier gas, a supply pipe 205 for organometal gases to be transferred by the carrier gas, a growth chamber 207 equipped with a heating mechanism 206, a gas discharge port 209, and so forth.

[0008]

The organometal materials 203 made ready in the bottle are, for example, strontium bis(dipivaloylmethanate) {abbr. $\text{Sr}(\text{DPM})_2$ }, barium bis(dipivaloylmethanate) {abbr. $\text{Ba}(\text{DPM})_2$ }, and lead bis(dipivaloylmethanate) {abbr. $\text{Pb}(\text{DPM})_2$ }, and maintain solid or liquid state at a normal temperature. In the CVD method using the apparatus, these organometal materials are sublimated in the bottle 202 and supplied to the growth chamber 207 while being accompanied with a carrier gas supplied from the supply pipe 204 to form a film on a heated wafer 208. The pressure during the film formation at that time is the atmospheric pressure or a pressure of several Torr.

15 [0009]

In the case such a method is employed, however, there is a disadvantageous point that the organometal gas flow rates in the carrier gas are difficult to be quantified and precisely controlled. That is because the carrier gas contains organometal gases in an amount equal to or more than the amount corresponding to the saturated vapor pressure determined by the temperature of the thermostatic tank 202 and because the flow rates of the organometal gases depend not only on the flow rate of the carrier gas but also on the surface area of raw material solids and the temperature of the thermostatic tank.

According to the description of Jpn. J. Appl. Phys. Vol.
32 (1993) P. 4175 on the formation of a film of PTO (lead
titanate: PbTiO_3) by the above film formation method, the
temperature of the formation of a PTO film is very high,
5 as high as 570°C , and the film obtained has a drawback
point that crystal orientation is uneven.

[0010]

In conventional production of a ferroelectric
memory or a DRAM, the foregoing film formation methods
10 are employed, however heating at a high temperature
around 600°C or higher in oxygen atmosphere is essential
and crystal orientation has been difficult to be
controlled.

[0011]

15 To give a description of a semiconductor in terms
of the structure, in order to make a ferroelectric
capacitor and a high-dielectric-constant capacitor well
functioning, it is required to electrically connect an
electrode of either one of capacitors to a diffusion
20 layer of a selective transistor. Conventionally, in a
DRAM, it is general that polysilicon connected to one
diffusion layer of a selective transistor is used as one
electrode and that a SiO_2 film, a Si_3N_4 film, or the like
is formed as a capacitive insulating film on the surface
25 of the polysilicon to compose the capacitor structure.
However, since the ceramic thin film is an oxide,

polysilicon is oxidized when the thin film is to be formed directly on the surface of the polysilicon and owing to that, it is impossible to form a good thin film. Hence, 1995 Symposium on VLSI Technology Digest of Technical Papers p. 123 describes a cell structure in which the upper electrode of a capacitor and a diffusion layer are connected by a local wiring of a metal such as Al or the like. Also, International Electron Devices Meeting Technical Digest, 1994 p. 843, describes a technique of forming a PZT capacitor on polysilicon using a TiN barrier metal. Regarding a DRAM, for example, International Electron Devices Meeting Technical Digest, 1994 p. 831, describes a technique of forming a STO (strontium titanate SrTiO_3) thin film on a RuO_2/TiN lower electrode form on a polysilicon plug to compose a capacitor.

[0012]

[Problem to be solved by the Invention]

However, the following problems exist in the foregoing film formation methods. A first problem is that since the crystallization temperature of the metal oxide dielectric film is as high as 600°C or higher, even if TiN is used as a barrier metal as described International Electron Devices Meeting Technical Digest p. 843, oxidation of TiN is inevitable and the contact resistance is increased. Further, it is also difficult

to use W and Al for a material of a plug instead of polysilicon. That is because W is easy to be oxidized and the temperature exceeds the melting point of Al. The practical upper limit temperatures of the respective
5 metals are around 500°C for TiN and around 450°C for W, Al.

[0013]

In Jpn. J. Appl. Phys. vol. 32 (1993) p. 4057, a sputtering method described is a method for controlling a
10 composition and lowering the crystallization temperature of PZT to 415°C by simultaneously sputtering multiple targets of respective constituent metal oxides. However, the sputtering method has problems that the method is inferior in coating on stepped surfaces and that the
15 method is difficult to be applied for film formation on side wall parts of a stack type or a trench type capacitor, and therefore, the method cannot be a countermeasure to a capacitor production technique for a semiconductor integrated circuit. Further, PLT is
20 paraelectric and the dielectric constant is low as compared with that of PZT. Therefore, most part of the voltage is applied to the PLT layer at the time of operating the device. This makes it hard to obtain ferroelectric properties at low voltage.

25 [0014]

A second problem is that the properties of a

dielectric film are deteriorated in the case of making the film thin. In order to achieve a high speed and make the structure ultrafine, it is essential to lower the voltage of a power source and in order to provide an electric field necessary for a capacitive insulating film, it is necessary to make the capacitive insulating film of the metal oxide dielectric film as thin as possible. Fig. 3 illustrates the film thickness and spontaneous polarization $2P_r$ in the case of forming a PZT film on Pt by a sol-gel method. In the case of 200 nm or thinner of the film thickness, the spontaneous polarization value is found sharply decreased. A similar phenomenon is also observed in the case of BST. There exists a problem that the dielectric constant of a BST film formed on RuO_2 by a CVD method is sharply decreased in the case of 50 nm or thinner of the film thickness. That is attributed to inferior crystallinity in the vicinity of the interface of a lower part electrode. Owing to the foregoing problems, conventional film formation methods are found difficult to make a capacitive insulating film thin and to lower the voltage of a power source.

A third problem is that the orientation of the film cannot be controlled. To make the orientation even is advantageous in the following points. At first, the grain boundaries of the polycrystal become continuous to lower the current leakage. Secondary, the dielectric

constant can be increased and the spontaneous polarization can be heightened by conforming the polarization direction to the electric field direction. [0015]

5 According to the description in Jpn. J. Appl. Phys. Vol. 32 (1993) P. 4075, it is described that PZT is epitaxially grown on a single crystal substrate of MgO(100) or Pt(100)/MgO(100) by a sputtering method and PZT significantly tends to be oriented to (001)
10 orientation. However, it is also described that orientation is uneven in the case where a film is formed on polycrystalline Pt oriented to (111) just like for the case of Pt(111)/Ti/SiO₂ and considering that the capacitor electrodes of a semiconductor integrated
15 circuit are polycrystalline, such a method cannot be a countermeasure.

 A fourth problem is a problem of inversion fatigue in the ferroelectric film. That is a phenomenon that the quantity of electric charge between inversion and non-
20 inversion is decreased if inversion of spontaneous polarization is repeated by applying voltage with sinusoidal or rectangular waveform to the ferroelectric film. Such a phenomenon is a serious problem which determinate the number of possible times of writing of a
25 ferroelectric capacitor and determinately affects the life in the case where a non-volatile memory is

fabricated using a ferroelectric material. However, as described in Jpn. J. Appl. Phys. Vol. 68 (1996) P. 1431, it is known that inversion fatigue occurs by inversion repeated only about 10^6 times in the case where Pt is
5 used for electrodes. A main memory like a dynamic random access memory (DRAM) is required to have a write life not less than 10^{11} times and a non-volatile memory using the ferroelectric material thus has a problem that the memory does not satisfy such a long write life.

10 A fifth problem is that the particle size of the polycrystalline PZT cannot be controlled. As the high density integration of the device proceeds further, the surface area of a capacitive part is lessened. To follow this, it becomes important to optimize the particle size
15 of a ceramic insulating film. In conventional examples, though the particle size is changed depending on the respective film formation methods, no effective method is reported to control the particle size in respective each film formation method.

20 [0016]

As described above, there are a lot of problems to be solved in formation of a thin film capacitor of a ceramic on a plug and in formation of a ceramic thin film capacitor on a multilayer metal wiring structure and thus
25 the cell surface area cannot easily be narrowed just like a conventional DRAM and a flash memory and consequently,

the integration degree has still been low, and the life was short.

[0017]

The present invention is developed while taking the
5 above described problems in conventional methods for
forming a capacitive insulation film of a ceramic into
consideration and aims at providing a vapor phase growth
method of a metal oxide dielectric film and capable of
forming a thin film excellent in both orientation and
10 crystallinity on a plug at a low temperature and further
aims at providing a semiconductor device made to have a
fine structure and a long life, highly integrated, and
multilayered and metallized.

[0018]

15 [Means for Solving the Problem]

The present invention relates to a vapor phase
growth method for carrying out film formation of a metal
oxide dielectric film with a perovskite type crystal
structure represented by ABO_3 on a conductive material
20 using organometal gases, comprising steps of: carrying
out initial nuclei formation of the perovskite type
crystal structure on the conductive material using all of
the organometal gases to be the raw materials of the
metal oxide dielectric film under first film formation
25 conditions, and carrying out film formation of the
perovskite type crystal structure further on the initial

nuclei under second film formation conditions.

[0019]

Further, the present invention relates to a vapor phase growth method for carrying out film formation of a metal oxide dielectric film with a perovskite type crystal structure represented by ABO_3 on a conductive material using organometal gases, comprising steps of: carrying out initial layer formation of the perovskite type crystal structure on the conductive material using all of the organometal gases to be the raw materials of the metal oxide dielectric film under first film formation conditions and carrying out film formation of the perovskite type crystal structure further on the initial layer under second film formation conditions.

[0020]

Further, the present invention relates to a vapor phase growth method for carrying out film formation of a metal oxide dielectric film with a perovskite type crystal structure represented by ABO_3 on a conductive material using organometal gases, comprising steps of: carrying out initial nuclei formation of the perovskite type crystal structure on the conductive material using only a part of the organometal gases to be the raw materials of the metal oxide dielectric film under first film formation conditions and carrying out film formation of the perovskite type crystal structure further on the

initial nuclei under second film formation conditions.

[0021]

Regarding the supply amounts of raw material gases in the first film formation conditions and the second
5 film formation conditions, it is preferable to control the second film formation conditions as to carry out film formation using raw material gas supply in good self-controlling conditions and also preferable to control the first film formation conditions so that the raw material
10 of the A element of the perovskite type crystal structure represented by ABO_3 is supplied in a higher quantity than that in the second film formation conditions

[0022]

In addition to that, it is preferable to control
15 the first film formation conditions as to relatively decrease the supply amount of Zr in the B element, in the case where the perovskite type crystal structure represented by ABO_3 contains Zr and Ti as the B element, as compared with that in the second film formation
20 conditions.

[0023]

Further, in an embodiment of the present invention, the first film formation conditions are so controlled as to supply no Zr raw material gas to carry out film
25 formation in the case the perovskite type crystal structure represented by ABO_3 contains Zr and other

elements as the B element.

[0024]

Further, in an embodiment of the present invention,
the film formation is carried out while controlling the
5 crystal grain size by controlling the initial nucleus
formation duration in the first film formation conditions.

[0025]

Further, in the present invention, it is preferably
to form a film in conditions where the total pressure of
10 the raw material gases including the organometal gases at
the time of film formation is kept at 1×10^{-2} Torr or
lower and the film formation temperature is kept at 450°C
or lower. The lower limit of the total pressure is not
specifically restricted but it is preferably at 1×10^{-4}
15 Torr or higher in order to obtain a practical film
formation rate.

[0026]

Incidentally, in the present invention, the film
formation temperature is preferably 450°C or lower.

20 [0027]

Further, an embodiment of the present invention is
characterized in that the metal oxide dielectric film is
a PZT film or BST film.

[0028]

25 Further, in an embodiment of the present invention,
the conductive material is a capacitor electrode

comprising at least any one of metals and metal oxides of Pt, Ir, Ru, IrO₂, RuO₂, TiN, and WN.

[0029]

Further, the present invention relates to a method
5 for fabricating a semiconductor device, comprising: a
step of forming a MOS-type transistor on a semiconductor
substrate, a step of forming a first interlayer
insulation film on the transistor, a step of forming
electric conduction by opening a contact reaching the
10 diffusion layer of the MOS-type transistor in the first
interlayer insulation film and burying a metal plug in
the contact, a step of forming a capacitor lower part
electrode layer on the whole surface of the first
interlayer insulation film having the metal plug, a step
15 of forming initial nuclei or an initial layer of a metal
oxide dielectric film having the perovskite type crystal
structure on the whole surface of the capacitor lower
part electrode layer using organometal gases under the
first film formation conditions and further forming the
20 metal oxide dielectric film having the perovskite type
crystal structure on the initial nuclei or the initial
layer under the second film formation conditions, a step
of forming a capacitor upper part electrode layer on the
whole surface of the metal oxide dielectric film, and a
25 step of patterning the capacitor lower part electrode
layer, the metal oxide dielectric film, and the capacitor

upper part electrode layer to obtain a capacitor with a three-layered laminated structure.

[0030]

Further, the present invention relates to a method
5 for fabricating a semiconductor device comprising: a step
of forming a MOS-type transistor on a semiconductor
substrate, a step of forming a first interlayer
insulation film on the transistor, a step of forming
electric conduction by opening a contact reaching the
10 diffusion layer of the MOS-type transistor in the first
interlayer insulation film and burying a metal plug in
the contact, a step of forming a capacitor lower part
electrode layer on the whole surface of the first
interlayer insulation film having the metal plug, a step
15 of forming a capacitor lower part electrode on the metal
plug by patterning the capacitor lower part electrode
layer, a step of forming initial nuclei or an initial
layer of a metal oxide dielectric film having the
perovskite type crystal structure on the whole surface of
20 the patterned capacitor lower part electrode and the
first interlayer insulation film layer using organometal
gases under the first film formation conditions and
further forming the metal oxide dielectric film having
the perovskite type crystal structure on the initial
25 nuclei or the initial layer under the second film
formation conditions, a step of forming a capacitor upper

part electrode layer on the whole surface of the metal
oxide dielectric film, and a step of patterning the
capacitor upper part electrode layer to obtain a
capacitor with a three-layered laminated structure of the
5 capacitor lower part electrode, the metal oxide
dielectric film, and the capacitor upper part electrode.
[0031]

Further, the present invention relates to a method
for fabricating a semiconductor device, comprising a step
10 of forming a MOS-type transistor on a semiconductor
substrate, a step of forming a first interlayer
insulation film on the transistor, a step of forming
electric conduction by opening a contact reaching the
diffusion layer of the MOS-type transistor in the first
15 interlayer insulation film and burying a metal plug in
the contact, a step of forming an aluminum wiring on the
first interlayer insulation film to electrically
connecting the aluminum wire with the metal plug, a step
of forming a second interlayer insulation film on the
20 aluminum wiring, a step of forming electric conduction by
opening a contact reaching the aluminum wiring in the
second interlayer insulation film and burying a metal
plug in the contact, a step of forming a capacitor lower
part electrode layer on the whole surface of the second
25 interlayer insulation film having the metal plug, a step
of forming initial nuclei or an initial layer of a metal

oxide dielectric film having the perovskite type crystal structure on the whole surface of the whole surface of the capacitor lower part electrode layer using organometal gases under the first film formation conditions and further forming the metal oxide dielectric film having the perovskite type crystal structure on the initial nuclei or the initial layer under the second film formation conditions, a step of forming a capacitor upper part electrode layer on the whole surface of the metal oxide dielectric film, and a step of patterning the capacitor lower part electrode layer, the metal oxide dielectric film, and the capacitor upper part electrode layer to obtain a capacitor with a three-layered laminated structure.

15 [0032]

The foregoing aluminum wiring may be multilayered.

[0033]

Further, in the vapor phase growth method of the present invention, the film formation conditions are changed to be first film formation conditions in which initial nuclei or an initial layer with the perovskite type crystal structure is formed on an electrode and successive second film formation conditions in which a film with the perovskite type crystal structure is formed on the formed initial nuclei or layer. In contrast, according to a conventional film formation method, film

formation on a conductive material has been carried out in same conditions through the process. In the present invention, it is also possible to select optimized conditions for the respective film formation conditions to carry out film formation. By carrying out film formation in such conditions, formation of a film with excellent in orientation property, crystallinity, and property relating inversion fatigue is made possible. [0034]

10 In general, the perovskite type crystal structure is represented by ABO_3 where the element A occupies site A and the element B occupies site B site. Incidentally, in some cases, a plurality of metal elements are contained as the A element and the B element of the
15 foregoing general formula. At the time of carrying out vapor phase growth of a metal oxide dielectric film having such a perovskite type crystal structure on a conductive material, in the case of film formation using all of the raw material gas seeds of elements
20 constituting a metal oxide dielectric film in first film formation conditions, a perovskite type crystal of either initial nuclei or an initial layer of crystallized some molecules in the film thickness direction is formed under the first film formation conditions. After that, a
25 crystal is further grown on the foregoing initial nuclei or the foregoing initial layer under the second film

formation conditions, which is raw material gas supply conditions enabling self-controlling film formation, so that a film with the perovskite type crystal structure and even orientation can be grown from the interface to the conductive material.

[0035]

The self-controlling film formation conditions mean raw material gas supply conditions to generate a perovskite type crystal structure whose composition spontaneously satisfies the stoichiometric ratios and whose orientation is made even. For example, the self-controlling film formation conditions in the case of PZT film formation will be described with reference to Fig. 18. This Fig. 18 illustrates the alteration of the composition ratio of (Ti + Zr)/Pb in films. Film formation of these films are first conducted for 40 seconds under the conditions of 0.2 SCCM flow rate of Pb(DPM)₂, 0.05 SCCM flow rate of Zr(OtBu)₄, 0.25 SCCM flow rate of Ti(OiPr)₄, and 3.0 SCCM flow rate of NO₂; and then the flow rate of the raw material for Pb was changed while constantly keeping the conditions of 0.225 SCCM flow rate of Zr(OtBu)₄, 0.2 SCCM flow rate of Ti(OiPr)₄, and 3.0 SCCM flow rate of NO₂. And the change of (Ti + Zr)/Pb in the resulting films was measured. The total pressure of the gases in a vacuum chamber during the film growth was controlled to be 5×10^{-3} Torr. A

substrate produced by forming a 200 nm thick Pt film on a silicon wafer bearing a 500 nm thick silicon oxide film thereon by sputtering was employed as a substrate. The duration of the film formation was set for 600 seconds and the thickness of the grown film was about 100 nm. The composition ratio were computed based on composition analysis by fluorescence x-rays. It was understood that the composition ratio reached the stoichiometric ratio when the flow rate of Pb was 0.15 SCCM; and that the stoichiometric ratio thereafter was kept by increasing the Pb flow rate even to 0.25 SCCM to prove formation of a crystal with a perovskite type crystal structure with even orientation. In such a manner, it can be understood that self-controlling film formation is possible to conform the composition of A, B sites, that is, Pb with Zr and Ti to the stoichiometric ratio in prescribed film formation conditions. That is based on the following principle. The Pb organometal gas is decomposed on the PZT surface and oxidized to PbO. The adhesion coefficient of PbO on the PZT is low and hence no film formation occurs only by passing the Pb organometal gas to the PZT surface. If Ti and Zr are supplied, PbO on the surface is bonded to Ti or Zr on the surface before being released to the vapor phase and immobilized on the surface. Consequently, even if a Pb raw material is supplied excessively to a certain extent, Pb which is not

bonded to Ti or Zr is released in gaseous phase to result in existence of a self-control region to give a stoichiometric ratio.

The most important point in film formation of a perovskite-type metal oxide dielectric film of such as PZT, BST, and the like on an electrode of Pt or Ir is generation of perovskite-type crystal nuclei on the substrate with a different crystal structure such as Pt or Ir. A perovskite-type metal oxide dielectric film on an electrode can be grown in the following manner. Raw material gases are decomposed at first on an electrode; precursors of constituent elements are adsorbed thereon; crystal nuclei are formed by integration of the precursors; the crystal nuclei are further grown to form an integrated layer-like form. Especially, at the time of crystal nucleus growth, the concentrations of the precursors of the constituent elements on the electrode surface are determined by the decomposition efficiency and the adhesion coefficient of each raw material on the base electrode and further by the diffusion of the raw materials into the electrode. It is, therefore, impossible to cause perovskite-type crystal nuclei formation if the concentrations on the surface are not conformed to the stoichiometric ratio of the substance to be grown to a film. The decomposition efficiency and the adhesion coefficient of each raw material gas on the

surface of base electrode are different from those on the surface of PZT crystalline; therefore even if the film formation conditions are so determined as to conform the stoichiometric ratio of the composition of the film after
5 thick film was formed, the composition formed on the base electrode at the moment of crystal nuclei formation, which is most important in the crystal growth, cannot be conformed to stoichiometric ratio. Therefore the crystallization does not take place.

10 [0036]

Further, inventors of the present invention have found that the element A to be disposed in the A site is easy to be alloyed with a conductive material composing an electrode and easy to be diffused in the electrode.
15 Consequently, in order to prevent deficiency of the A element in the vicinity of the interface by diffusion, it is necessary to supply a rather large amount of the A element in the first film formation conditions. The amount of the A element in the first film formation
20 conditions can be increased so that the supply ratio of A element to that of B element may be increased by about 10 times of the ratio prescribed in the second film formation conditions which are self-controlling gas supply conditions of the film formation. In the case of
25 multiple element system in which the A element or the B element is composed of a plurality of elements, the

increased amount is determined by the total of the supply amounts of these elements. For example, in the case of PZT film formation as shown in Figs. 4, inventors of the present invention optimized the first film formation conditions for generation of nuclei of PZT on the electrode by increasing the supply amount of the Pb raw material more than that of the second film formation conditions of self-controlling film formation of PZT on the PZT crystal nuclei. Thus, the generation of crystal nuclei 702 on an electrode is carried out by conforming the concentrations of the precursors 701 of constituent elements on the electrode surface to the stoichiometric ratio. Thereafter, excellent crystal growth on the crystal nuclei 702 is carried out.

15 [0037]

That is, Pb, which is the A element of the constituent elements, most easily causes reaction with the base electrode and is easily removed from the electrode. The reaction of Pb with the base electrode is determined by the film formation temperature and the electrode materials and since the film formation temperature is increased more, the reaction with the electrode is intensified more, the supply amount of Pb is required to be increased more in the film formation conditions during generating PZT nuclei. Further, since Pt, as compared with Ir and Ru, has high reactivity to Pb,

a further more Pb raw material is required to be supplied in the case of using Pt as the conductive material. In the case of forming BST, in the same manner, a Ba raw material has to be supplied more, though it is not so much as in the case of Pb.

[0038]

Inventors of the present invention have found that more excellent PZT crystal nuclei were formed by lessening a Zr raw material in comparison with a Ti raw material in the case of using both of Zr and Ti as the B element. That is because the decomposition efficiency of the Zr raw material on an electrode is high as compared with that of the Ti raw material.

[0039]

Though described above is the description of the case of formation of a perovskite-type metal oxide dielectric material represented by ABO_3 , the same method can be applied for materials with other structures. That is, to supply an element most easily alloyed with an electrode material or diffused in the electrode material in a large amount in the initial period of the growth is effective to film formation of any kind of compounded metal oxides.

[0040]

Further, inventors of the present invention have found that, in the case of carrying out generation of

initial nuclei of perovskite type crystal structure represented by ABO_3 , the initial nuclei formation is carried out using a part of raw material gases of especially the A element or the B element and then film
5 formation is carried out further on the initial nuclei under the second film formation conditions. That is because, at the time of initial nucleus formation, a substance with a simpler composition is easy to control the film formation conditions to cause perovskite type
10 nuclei generation.

[0041]

Inventors of the present invention have found that, when a PZT film is formed, the first film formation conditions can be easily controlled when the nuclei
15 generated have a simple binary composition of PTO; and that when BST is formed, the first film formation conditions can be easily controlled when the nuclei generated have a simple binary composition of BTO. That is because the control of the composition ratio can be
20 performed by controlling especially only two elements. However as shown in Figs. 4, the important point in nuclei formation is that the film formation of PZT or BST has to be carried out by changing the film formation conditions to the second film formation conditions in
25 self-controlling regions before the formed nuclei becomes a continuous film. The reason for that is if a

continuous film is formed, an insulation film with a different composition and a different dielectric constant is formed in the interlayer to an electrode, which causes unevenness of an electric field in the film and decreases the dielectric constant of the film. Once perovskite type crystal nuclei 702 are formed on the electrode, the precursors 701 of the constituent elements are grown to form a film around the crystal nuclei in the self-controlling manner, so that an excellent crystal can be obtained by changing the conditions to the second film formation conditions in which PZT film formation on the crystal nuclei takes place in the self-controlling manner. Further, inventors of the present invention have found that the crystal grain size of a metal oxide dielectric film grown on initial nuclei can be controlled by controlling the duration period of the initial nuclei formation in the first film formation conditions and, in order to control the crystal grain size in such a manner, the first film formation conditions have to be restricted only to the stage of the initial nuclei formation.

[0042]

Incidentally, the organometal gases mean raw material gases of organometals necessary to form a desired ferroelectric film or a high-dielectric-constant film on a capacitor electrode. For example, in the case of a PTZ film, examples of the organometal gases include

gases of lead bis(dipivaloylmethanate) ($\text{Pb}(\text{DPM})_2$),
tetra(tert-butoxy) zirconium ($\text{Zr}(\text{OtBu})_4$),
tetra(isopropoxy) titanium ($\text{Ti}(\text{OiPr})_4$), and the likes.
In the case of a BST film, examples include gases of
5 barium bis(dipivaloylmethanate) ($\text{Ba}(\text{DPM})_2$), strontium
bis(dipivaloylmethanate) ($\text{Sr}(\text{DPM})_2$), tetra(isopropoxy)
titanium ($\text{Ti}(\text{OiPr})_4$), and the likes. Additionally, it is
preferable to use an oxidizing gas, besides the
organometal gases, to sufficiently oxidize the
10 organometal gases to avoid alloying of the gases on a
conductive material and to prevent oxygen deficiency and
nitrogen dioxide, ozone, oxygen, oxygen ion, and oxygen
radical can be used as the oxidizing gas. Among these,
nitrogen dioxide is preferable because this has the
15 highest oxidizing force.
[0043]

Inventors of the present invention have found that
the film formation at a low temperature is possible by
controlling the total pressure to be 1×10^{-2} Torr or
20 lower at the time of film formation in the case of
forming a metal oxide dielectric film on a capacitor
electrode using organometal gases and further that the
film formation of a highly excellently oriented film is
possible.
25 [0044]

That is, within the foregoing pressure range, even

at a temperature of 450°C or lower, approximately 100% of PZT has been found oriented in the PZT(100) direction.

The temperature is, as compared with the film formation temperature of a conventional method, a low film

5 formation temperature by about 150°C or more.

Consequently, for example, film formation can be carried out without oxidation of W, TiN or the like formed in the contact plug and fusion of an Al wiring formed on a

substrate. As a result, by a vapor phase growth method

10 of the present invention, a metal oxide dielectric film with uniform orientation can be formed on a semiconductor substrate on which a TiN or W layer and an Al wiring is formed.

[0045]

15 The reason why a crystal with uniform orientation is formed without increasing the temperature, inventors of the present invention presume as follows. Inventors of the present invention suppose whether formation of a crystal with uniform orientation is possible or not

20 depends on the frequency of the collision of molecules of organic metal gases and an oxidizing gas. That is, if the total pressure of a vacuum chamber is 1×10^{-2} Torr or higher, molecules of organic metal gases and an oxidizing gas repeat collision a large number of times before they
25 reach the substrate and fine crystals with uncontrolled compositions are formed and the fine crystals become

causes of disorder of the crystal structure and therefore,
it can be supposed that if the pressure is in a range of
 1×10^{-2} Torr or lower, such fine crystal formation can
practically be suppressed and the crystal structure tends
5 to easily be uniform even at a low temperature.

[0046]

However, in order to obtain a practically
applicable film formation rate, the film formation is
preferable to be carried out at higher than 1×10^{-4} Torr
10 and most preferable to be carried out at a pressure
within a range from 1×10^{-3} Torr to 1×10^{-2} Torr.

[0047]

In the present invention, on a conductive material
is formed a strong dielectric film or a high electric
15 film, which is a metal oxide dielectric film, preferably
including a PZT film and a BST film.

[0048]

Conductive materials to be employed for the present
invention include metals such as Pt, Ir, Ru, TiN, WN, and
20 the likes and metal oxides such as IrO_2 , RuO_2 , and the
likes. These are employed for capacitor electrode. In
the case of Pt as a conductive material, if the Pt is
layered on TiN layered on Ti with a Pt/TiN/Ti structure,
TiN functions as a barrier to suppress diffusion of Ti.
25 Further, since TiN of the structure has a crystal
structure highly oriented to (111), Pt is also oriented

to (111). However, being different from a conventional film formation method, a vapor phase growth method of the present invention has been found having an advantageous point that a metal oxide dielectric film is easy to be
5 oriented and to be provided with excellent crystallinity. In a contact plug, W is also commonly used and a Pt/TiN/Ti/W structure, which is produced by further forming a W layer in the lower layer of the foregoing structure can also be used preferably for a conductive
10 material for the present invention.

[0049]

[Modes of Execution]

Hereafter, an embodiment of the present invention will be described with reference to Figs.

15 [0050]

A schematic diagram of one example of a thin film vapor phase growth apparatus to be employed for the present invention is illustrated in Fig. 5. The present apparatus is composed of an exchange chamber 101, a
20 vacuum chamber 102, and a raw material supply system 103 and a plurality of sheets of 8-inch wafers can be housed in the exchange chamber. Double gate valves 104 are installed between the vacuum chamber and the exchange chamber and the space between the two gate valves is
25 evacuated by a pump. A wafer transferring mechanism 105 is installed for transferring wafers between the vacuum

chamber and the exchange chamber. With such a constitution, wafers can be replaced and transferred without the vacuum chamber being exposed to atmospheric air. Further, the double insertion of the gate valves is effective to suppress adhesion of the raw materials to the valve seal face and prevent leakage of atmospheric air in the vacuum chamber at the time of atmospheric air leak in the exchange chamber for replacing wafers. The exchange chamber is evacuated to 10^{-7} Torr by turbopumps 106 independently installed from the pump for the vacuum chamber.

[0051]

A schematic diagram showing a part of the cross-section of the vacuum chamber is illustrated in Fig. 1. The vacuum chamber is equipped with a heater denoted with 416 and made of aluminum to be heated to a prescribed temperature. The material of the vacuum chamber is preferable to have a high thermal conductivity and, especially, aluminum. By using aluminum, the inner walls of the vacuum chamber can evenly be heated.

Wafers 417 are so set on a susceptor 403 made of quartz as to keep the faces to be subjected to device formation upward. Three holes 401 with 5 mm diameter are formed in the susceptor 403 made of quartz and pins 402 made of quartz are moved up and down through the holes to mount wafers on the susceptor 403 from the transferring

apparatus. After the wafers are mounted on the susceptor made of quartz, the holes for the pins are closed by the wafers themselves. The susceptor is so put on projections projected from a wall of a vacuum chamber made of aluminum as to overlap the rim parts on the projections and in the state in which the wafers are mounted on the susceptor made of quartz, the heater chamber 405, a lower part of the wafers, and the vacuum chamber 406, an upper part, into which film growth gases are to be introduced are separated.

[0052]

The inner walls of the vacuum chamber 406 are preferable to be set at a temperature not lower than a temperature at which organometal gases can have sufficiently high vapor pressures and not higher than organometal gas decomposition temperature. That is, since organometal gases include several kinds of raw materials, the composition ratio of organometal gases reacting on the wafer could be unbalanced owing to that a part or all of the organometal gases are liquefied or solidified or that organometal gases are decomposed, so that the temperature is preferable to be controlled not lower than the temperature at which the organometal gases have sufficiently high dissociation speed without being condensed in the inner wall and lower than the decomposition temperature of the organometal gases.

[0053]

The vacuum chamber 406 and the heater chamber 405 are evacuated by separate turbo molecular pumps 407, 408 and with such a structure, the leakage of organometal
5 gases and an oxidizing gas to the heater chamber can be suppressed. Especially, in the case of this growth method using an oxidizing gas, oxidation of the heating mechanism 409 installed in the heater chamber to heat wafers can be prevented and thus the life of the heating
10 mechanism 409 can significantly be prolonged. Such a structure is also effective to prevent short circuit and to prevent unevenness of the substrate temperature caused by adhesion of raw material gases on the heating mechanism. The pressure of the heater chamber during the
15 film formation was 1×10^{-6} Torr when the pressure of a vacuum chamber was 1×10^{-3} Torr and the pressure difference of about three figures was obtained.

[0054]

When the temperature of a heater for heating wafers
20 is increased, the temperature of a susceptor made of quartz is also increased to cause adhesion of organometal gases thereon, however by coating the surface of quartz with a metal oxide (a high temperature part-coating dielectric material) of such as STO (strontium titanate:
25 SrTiO_3), the parting of adhering substances of organometal gases can be suppressed and as a result,

contamination with particles can be prevented. As the high temperature part-coating dielectric material, the preferable compounds are, besides STO, PTO (lead titanate: PbTiO_3), BTO (barium titanate: BaTiO_3), PLZT 5 $\{(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3\}$, PNBZT $\{(\text{Pb}, \text{Nb})(\text{Zr}, \text{Ti})\text{O}_3\}$, SBT $(\text{SrBi}_2\text{TaO}_9)$, $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$, $(\text{Ba}, \text{Sr})\text{TiO}_3$, and the likes. [0055]

Two lines, a main exhaust line 410 and a sub exhaust line 411, are connected to an exhaust port of a vacuum chamber and the main exhaust line is connected to 10 a turbo pump 407 through a main gate valve 412. The sub exhaust line 411 is connected to the turbo pump 407 through a valve 413 and then a water cooling trap 414. During the film formation, the main gate valve 412 is 15 closed and the valve 413 is opened to discharge exhaust gases through the sub exhaust line 411. With such a constitution, solidification and liquefaction of organometal gases in the turbo pump 407 can be avoided and the life of the turbo pump 407 can be prolonged. 20 Additionally, the total pressure of raw material gases in the vacuum chamber can be changed by introducing a valve 415 capable of adjusting conductance between the sub exhaust line 411 and the water cooling trap 414 and adjusting the conductance. At the time when no raw 25 material gas is supplied, the exhaust speed can be heightened by opening also the main gate valve 412 to

effectively maintain high vacuum degree. The main gate valve 412 and the valve 413 are buried in an aluminum vacuum chamber 406 and enabled to be evenly heated.

In this apparatus, though a turbo molecular pump is employed for a pump for exhaust, a mechanical booster pump, a dry pump, a rotary pump, or the like may be usable and it is required to plan the exhaust capability of the pump and conductance of the valves and the water cooling trap as to decrease the inner pressure of the vacuum chamber to 1×10^{-2} Torr or lower.

[0056]

A schematic diagram of a part of a raw material supply system is illustrated in Fig. 6. An organometal gas is a solid or a liquid at a room temperature and stored in a cylinder 501. The cylinder 501 is equipped with a valve 502 installed above and enabled to be parted from a flange 503 between the valve 502 and the supply system to exchange raw materials. Each organometal gas is extremely easily oxidized, so that the organometal gas is preferable to be kept no contact with atmospheric air. If being exposed to atmospheric air, the organometal gas is oxidized, a metal oxide is formed, the pipes are clogged, and a mass flow controller 504 is clogged.

[0057]

Organometal gases include those in a liquid state and those in a solid state at a normal temperature and

normal pressure and the liquid raw materials are poured in cylinders as they are. On the other hand, solid raw materials are preferable to be deposited on the surface of alumina with about 1 mm diameter. By using such raw materials, gases can be generated stably at the time of heating. The purity of the generated gases is high. The heating temperature of a cylinder is set to be a temperature high enough to obtain a sufficiently high vapor pressure to operate the mass flow controller.

10 [0057]

A pipe from the cylinder 501 is connected to the mass flow controller 504 through a stop valve 505 and thereafter divided into two pipes equipped with stop valves 506, 507, respectively, and connected to a vacuum chamber 508 and to a pump 512 via a water cooling trap 509, respectively. Parts of the raw material supply system comprising these pipes, the mass flow controller 504, valves 502, 505, 506, 507, and the likes and which are to be brought into contact with organometal gases are, as the same as the inner walls of the foregoing vacuum chamber, kept at a temperature not lower than the temperature at which the organometal gases are liquefied or solidified and not higher than the decomposition temperature of each organometal gas.

25 In an apparatus to be employed for the present invention, the flow rate of each raw material gas is

adjusted by a mass flow controller and that is because it is preferable to directly control the flow rate of each raw material gas without using a carrier gas and from that point of view, flow rate control is not limited to
5 that by a mass flow controller.

[0059]

At the time of film formation, at first the valve 502, 505, 506 are opened to operate the mass flow controller 504 by the spontaneous pressure of an
10 organometal gas in the cylinder 501 and a gas is evacuated by the pump 512 to stabilize the gas flow rate in the mass flow controller 504 during the time. Next, the valve 506 is closed and the valve 507 is opened, so that the organometal gas whose flow rate is precisely
15 controlled can be supplied to the vacuum chamber.

Each of organometal gases and an oxidizing gas is introduced into a vacuum chamber through independent raw material supply pipes and then mixed to one another in the vacuum chamber. That is, the apparatus is so
20 composed as to keep separated of the organometal gases and the oxidizing gas from each other before they are introduced into the vacuum chamber. The reason for that is, because if the organometal gases and the oxidizing gas are brought into contact with each other, the
25 organometal gases are oxidized and metal oxides are generated to cause clogging of the pipes and clogging of

the mass flow controller and further because the metal oxides are sent to the vacuum chamber to result in generation of particles and inhibition of thin film formation with excellent crystallinity at low temperature.

5 [0060]

The partial pressure of each organometal gas in the vacuum chamber is determined by the supply amount of each gas, the amount consumed on the substrate and the susceptor, the exhaust amount, and the adhesion amount to
10 the walls of the vacuum chamber. If the temperature of the walls of the vacuum chamber is kept at a proper temperature to keep a sufficiently high vapor pressure of each organometal gas and to inhibit decomposition of each organometal gas, the decrease owing to the adhesion of
15 the raw material gases to the inner walls of the vacuum chamber can be neglectable. Further since the raw material gas amount consumed on the substrate and the susceptor is as low as about 1/1000 of the supply amount, the pressure of the vacuum chamber is determined by the
20 gas supply amount and the exhaust amount. A vacuum gauge 510 for monitoring the pressure is installed in the vacuum chamber. Incidentally, the foregoing parts which are to be brought into contact with organometal gases are required to be parts having sufficiently high heat
25 resistance to the temperature at which at least organometal gases can have sufficient vapor pressure.

[0061]

By providing an apparatus with the above described apparatus constitution, only organometal gases and an oxidizing gas necessary for film formation can be introduced into the vacuum chamber to actualize the film formation conditions of the present invention. That is, an oxidizing gas and each organometal gas can be introduced into the vacuum chamber through separate introduction ports and the pressure can be controlled to keep the inner pressure of the vacuum chamber at 1×10^{-2} Torr or lower. The pressure of the vacuum chamber may be changed and adjusted to be at a desired value by adjusting the exhaust amount of the sub exhaust line 411 and the flow rate of the mass flow controller. Further, by adjusting the temperature of the heater 416 to be at a prescribed temperature, it is made possible to control the temperature of the inner walls of the vacuum chamber not lower than the temperature at which the organometal gases have sufficiently high vapor pressure and lower than the decomposition temperature of the organometal gases. In this apparatus example, aluminum, which is a material having a high thermal conductivity, is used as a material for the vacuum chamber and if the temperature to provide sufficient vapor pressure of organometal gases exceeds 200°C, a stainless steel may be employed.

[0062]

Further, since the mass flow controller is operated by the spontaneous pressure of raw material gases and the likes to introduce organometal gases and the oxidizing gas into the vacuum chamber, not like a conventional
5 method, raw materials can be transported without using a carrier gas.

[0063]

In a method for vapor phase growth on a capacitor electrode using organometal gases, nitrogen dioxide may
10 be used as the oxidizing gas. Nitrogen dioxide may be passed through a pipe for the oxidizing gas.

[0064]

The total pressure of the vacuum chamber during the film formation can be kept at 1×10^{-2} Torr or lower by
15 controlling the exhaust amount of the sub exhaust line 411 (Fig. 1) and the flow rate of the mass flow controller 504 (Fig. 6).

[0065]

Next, an embodiment of a film formation method of
20 the present invention will be described while exemplifying film formation of a PZT film, for example.

[0066]

Next, an embodiment of a film formation method of the present invention will be described while
25 exemplifying film formation of a PZT film, for example.

[0067]

Representative raw materials, raw material temperature, and temperature of a mass flow controller in the case of PZT film formation are as follows: as a Pb raw material, lead bis(dipivaloylmethanate) $\text{Pb}(\text{DPM})_2$, raw material temperature 177°C, temperature of a mass flow controller 200°C; as a Zr raw material, tetra(tert-butoxy) zirconium $\text{Zr}(\text{OtBu})_4$, raw material temperature 70°C, temperature of a mass flow controller 110°C; as a Ti raw material, tetra(isopropoxy) titanium $\text{Ti}(\text{OiPr})_4$, raw material temperature 75°C, temperature of a mass flow controller 145°C; the mass flow temperature of NO_2 145°C; and the temperature of the inner walls of the vacuum chamber 180°C.

[0068]

- 15 Fig. 7 is an x-ray spectrum in the case of forming a 100 nm PZT film at 500°C film formation temperature and for 600 seconds in conditions of 0.25 SCCM flow rate of $\text{Pb}(\text{DPM})_2$, 0.225 SCCM flow rate of $\text{Zr}(\text{OtBu})_4$, 0.2 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$, and 3.0 SCCM flow rate of NO_2 .
- 20 Fig. 8 is an x-ray spectrum in the case of forming a 100 nm PZT film at 500°C film formation temperature in conditions at first of 0.2 SCCM flow rate of $\text{Pb}(\text{DPM})_2$, 0.05 SCCM flow rate of $\text{Zr}(\text{OtBu})_4$, 0.25 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$, and 3.0 SCCM flow rate of NO_2 for 40 seconds
- 25 and then in conditions of 0.25 SCCM flow rate of $\text{Pb}(\text{DPM})_2$, 0.225 SCCM flow rate of $\text{Zr}(\text{OtBu})_4$, 0.2 SCCM flow rate of

Ti(OiPr)₄, and 3.0 SCCM flow rate of NO₂ for 600 seconds. Silicon wafers employed for substrates were those produced by forming a 500 nm thick silicon oxide film on silicon wafers and then forming a 200 nm thick Pt film by a sputtering method. In comparison of Fig. 7 and Fig. 8 to each other, only the peak of Pt was observed in Fig. 7 showing that no PZT crystallization took place, whereas peaks of (100), (200) of PZT were observed in Fig. 8 showing that it was effective to carry out film formation by altering the flow rates in two stages as described above to form a perovskite type film with excellent crystallinity.

[0069]

Table 1 shows the proper flow rates of Pb, Zr, and Ti raw materials separately for the initial nuclei formation time and film formation time in the case of forming Pb(Zr_{0.5}Ti_{0.5})O₃ on Pt, Ir, Ru, IrO₂, and RuO₂ at 400°C substrate temperature. In the case of carrying out film formation on Pt, as compared with the cases of film formation on Ir, Ru, IrO₂, and RuO₂, that the Pb flow rate is high at the time of the initial nuclei formation is because, as for Pt, diffusion coefficient of Pb into Pt is high and subsequently, the Pb concentration on the surface is decreased by the diffusion. Diffusion of Pb into Ir, Ru is scarce. The optimum film formation conditions are all the same after the perovskite nuclei

are generated and successively the electrode surface is coated with PZT. Table 2 shows the proper flow rates of Pb, Zr, and Ti raw materials separately for the initial nuclei formation time and film formation time in the case of forming $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ on Pt, Ir, Ru, IrO_2 , and RuO_2 by carrying out at first nuclei formation using PTO and successively forming PZT. Also in this case, the Pb flow rate is low at the time of initial nuclei formation on Ir, Ru, IrO_2 , and RuO_2 . The reason for that is also because Pb is diffused much into Pt. In the case of a Pt/Ti layered structure, the Ti concentration on the surface is increased since Ti is diffused and appears on the Pt surface at the time of heating and therefore, in order to carry out nuclei formation, it is required to lower the Ti supply amount as compared with that in the case no Ti exists under Pt. By forming a Pt/TiN/Ti structure, Ti diffusion can be suppressed by TiN and the crystallinity of Pt on the TiN is provided with a structure oriented highly to (111), so that the crystallinity and orientation property of PZT can be improved and the initial nuclei generation can easily be controlled. Film formation can also be carried out on a Pt/ SiO_2 structure in the same manner.

[0070]

[Table 1]

Conductive material	First film formation conditions (SCCM)				Second film formation conditions (SCCM)			
	Gas flow rate of Pb raw material	Gas flow rate of Zr raw material	Gas flow rate of Ti raw material	Gas flow rate of NO ₂ raw material	Gas flow rate of Pb raw material	Gas flow rate of Zr raw material	Gas flow rate of Ti raw material	Gas flow rate of NO ₂ raw material
Pt	0.25	0.1	0.15	3.0	0.2	0.225	0.25	3.0
Ir	0.2	0.15	0.15	3.0	0.2	0.225	0.25	3.0
Ru	0.2	0.15	0.15	3.0	0.2	0.225	0.25	3.0
IrO ₂	0.25	0.1	0.15	3.0	0.2	0.225	0.25	3.0
RuO ₂	0.25	0.1	0.15	3.0	0.2	0.225	0.25	3.0

[0071]

5 [Table 2]

Conductive material	First film formation conditions (SCCM)				Second film formation conditions (SCCM)			
	Gas flow rate of Pb raw material	Gas flow rate of Zr raw material	Gas flow rate of Ti raw material	Gas flow rate of NO ₂ raw material	Gas flow rate of Pb raw material	Gas flow rate of Zr raw material	Gas flow rate of Ti raw material	Gas flow rate of NO ₂ raw material
Pt	0.25	0	0.25	3.0	0.2	0.225	0.25	3.0
Ir	0.2	0	0.25	3.0	0.2	0.225	0.25	3.0
Ru	0.2	0	0.25	3.0	0.2	0.225	0.25	3.0
IrO ₂	0.25	0	0.25	3.0	0.2	0.225	0.25	3.0
RuO ₂	0.25	0	0.25	3.0	0.2	0.225	0.25	3.0

As shown above, in the case of film growth at the same temperature, it is required to control the flow

rates at the time of initial perovskite nuclei formation depending on the difference of the electrodes. The gas decomposition efficiency, the adhesion coefficient, the diffusion coefficient in relation to the electrode surfaces and further the gas decomposition efficiency, the adhesion coefficient, the diffusion coefficient in relation to PZT are also changed by the film formation temperature. Fig. 9 shows the composition ratios of Ti/Pb and Zr/Pb in the case of changing only the film formation temperature in 100 nm thick PZT film formation on Pt/SiO₂ carried out in the prescribed film formation conditions: at first for 40 seconds in the conditions of 0.2 SCCM flow rate of Pb(DPM)₂, 0.05 SCCM flow rate of Zr(OtBu)₄, 0.25 SCCM flow rate of Ti(OiPr)₄, and 3.0 SCCM flow rate of NO₂ and then further for 100 seconds in the conditions of keeping 0.25 SCCM flow rate of Pb(DPM)₂, 0.225 SCCM flow rate of Zr(OtBu)₄, 0.2 SCCM flow rate of Ti(OiPr)₄, and 3.0 SCCM flow rate of NO₂. According to Fig. 26, the composition is changed following the alteration of the substrate temperature. Consequently, also in the case of altering the substrate temperature, It is required to select the optimum initial nuclei generation conditions and growth conditions.

[0072]

Fig. 10 shows x-ray diffraction spectra in the case of optimizing the film formation conditions for the

respective stages and changing the film formation temperature. Silicon wafers employed for substrates were those produced by forming a 500 nm thick silicon oxide film on silicon wafers and then forming a 200 nm thick Pt
5 film by a sputtering method. Film formation was carried out in conditions at first of 0.2 SCCM flow rate of $\text{Pb}(\text{DPM})_2$, 0.05 SCCM flow rate of $\text{Zr}(\text{OtBu})_4$, 0.25 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$, and 3.0 SCCM flow rate of NO_2 for 40 seconds and then in conditions of 0.25 SCCM flow rate
10 of $\text{Pb}(\text{DPM})_2$, 0.225 SCCM flow rate of $\text{Zr}(\text{OtBu})_4$, 0.2 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$, and 3.0 SCCM flow rate of NO_2 for 600 seconds. The total pressure of the gases in a vacuum chamber during the film growth was controlled to be 5×10^{-3} Torr.

15 [0073]

As being understood from Figs. 8, x-ray diffraction peak attributed to PZT with the perovskite type crystal structure were observed at 400°C substrate temperature. Though being not shown in Fig. 10, no peak attributed to
20 PZT was observed at all at 350°C substrate temperature and it was found that the film was in amorphous state. In the present invention, film formation is preferable to be carried out at 360°C or higher and, for example, at 380°C, a PZT film with sufficiently evenly oriented
25 crystal structure was obtained. In this Figs., the x-ray diffraction spectra obtained in the case of employing

film formation temperature at three levels; 400°C, 500°C, and 600°C were compared to one another. As being shown in the Figs., in a high temperature region of 500°C or higher, two kinds of peaks of (100) and (101) were
5 observed, whereas in a low temperature region of around 400°C, only one kind peak of (100) was observed, implying that to form a film at a low temperature was effective to obtain a film with extremely even crystallization direction and with a highly oriented perovskite type
10 crystal structure. Also in the case of forming a film at a temperature lower than 400°C, as long as the temperature was high enough to form a perovskite type crystal structure, the patterns of the x-ray diffraction spectra of the resultant films were same as those of
15 films formed at 400°C and only one kind peak of (100) was observed to find that films formed had extremely even crystallization direction and with a highly oriented perovskite type crystal structure.

[0074]

20 The present invention is also significantly effective to improve property deterioration at the time of making a film thin. That is based on the following principle. By a conventional method such as a sol-gel method or the like, crystallization is caused by heating
25 at a temperature as high as 600°C or higher. At that time, metals in the ceramics are alloyed with an

electrode metal and diffused in the electrode metal.
Thus a part of the interface between the electrode and
the ceramic insulation layer is deficient in a metal.
Such a part where a part of metals is lessened is called
5 as a transition layer. The transition layer has a
composition deviated from the stoichiometric ratio to
result in inferior electric properties. In the case
where a film is made thin, the ratio of the transition
layer in the film increases to result in deterioration of
10 properties. However, in this method of the present
invention, since film formation is carried out at 450°C
or less, such a transition layer is scarcely formed and
deterioration of the properties in the case of thinning a
film is scarce.

15 [0075]

Fig. 11 shows the dependency of the spontaneous
polarization on the film thickness, where PZT film
formation was conducted by a vapor phase growth method of
the present invention. Silicon wafers employed for
20 substrates were those produced by forming a 500 nm thick
silicon oxide film on silicon wafers and then forming a
200 nm thick Pt film by a sputtering method. The film
formation conditions were controlled as follows: film
formation was carried out at first for 40 seconds in the
25 conditions of 0.2 SCCM flow rate of $\text{Pb}(\text{DPM})_2$, 0.05 SCCM
flow rate of $\text{Zr}(\text{OtBu})_4$, 0.25 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$,

and 3.0 SCCM flow rate of NO_2 , and then film formation was carried out for 600 seconds in the conditions of 0.25 SCCM flow rate of $\text{Pb}(\text{DPM})_2$, 0.225 SCCM flow rate of $\text{Zr}(\text{OtBu})_4$, 0.2 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$, and 3.0 SCCM flow rate of NO_2 . The total pressure of the gases in a vacuum chamber during the film growth was controlled to be 5×10^{-3} Torr. The obtained film thickness in this case was 100 nm. As compared with results of spontaneous polarization of a dielectric film formed by a sol-gel method as shown in Fig. 3, it was found that the spontaneous polarization value did not decrease even in the case of thin films. The similarly improvement effect was confirmed in suppression of specific dielectric constant in a high-dielectric-constant film of such as BST.

[0076]

A method of the present invention is also significantly effective to improve inversion fatigue strength. It also based on the same principle as that in the case of the improvement of property deterioration at the time of making a film thin. It is known that the inversion fatigue in the interface between an electrode and a ferroelectric thin film is attributed to the pin stop effect of electric charge. Therefore, the inversion fatigue strength can be improved by heightening the perfection of the interface by lessening the transition

layer in the interface. Fig. 12 shows the dependency of spontaneous polarization on the number of inversion times in the case of PZT film formation by a vapor phase growth method of the present invention. Silicon wafers employed
5 for substrates were those produced by forming a 500 nm thick silicon oxide film on silicon wafers and then forming a 200 nm thick Pt film by a sputtering method. Film formation was carried out at 400°C substrate temperature in conditions at first of 0.2 SCCM flow rate
10 of $\text{Pb}(\text{DPM})_2$, 0.05 SCCM flow rate of $\text{Zr}(\text{OtBu})_4$, 0.25 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$, and 3.0 SCCM flow rate of NO_2 for 40 seconds and then in conditions of 0.25 SCCM flow rate of $\text{Pb}(\text{DPM})_2$, 0.225 SCCM flow rate of $\text{Zr}(\text{OtBu})_4$, 0.2 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$, and 3.0 SCCM flow rate of NO_2 for
15 600 seconds. The grown film thickness was 100 nm. Spontaneous-polarization was measured by forming 200 nm thick Pt film as an upper part electrode by sputtering, separating by etching, and then measuring the polarization between the upper part and lower part
20 electrodes by Sawyer Tower circuit. According to Fig. 12, no fatigue was observed even after inversion repeated 10^{11} times and the method of the present invention was found effective to improve the inversion fatigue strength.
[0077]

25 A method of the present invention is also applicable for grain size control. That is based on the

following principle. When film formation is carried out in the initial nuclei formation conditions, just as shown in Fig. 4, island-like perovskite crystal nuclei are formed on the electrode. The density of the crystal nuclei is proportional to the duration time of the initial nuclei growth. Then, when the film formation is carried out by changing from the nuclei formation conditions to the film formation conditions, crystal growth takes place mainly on these crystal nuclei. Therefore, a polycrystal having the same crystalline-density as that of the nuclei initially formed on the electrode can be produced. That is, if the nuclei density (i.e. number of nuclei) on the electrode is lowered by shortening the nuclei formation duration time, the grain size finally obtained becomes large. If the nuclei density is increased by prolonging the nuclei formation time, the grain size finally obtained becomes small. Fig. 13 shows the correlation of the duration of the initial nuclei formation and the grain size of PZT in the case of changing the duration of the initial nuclei formation from 15 seconds to 100 seconds in film formation carried out at 400°C substrate temperature in conditions at first of 0.2 SCCM flow rate of $\text{Pb}(\text{DPM})_2$, 0.05 SCCM flow rate of $\text{Zr}(\text{OtBu})_4$, 0.25 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$, and 3.0 SCCM flow rate of NO_2 for nuclei formation and then in conditions of 0.25 SCCM flow rate

of $\text{Pb}(\text{DPM})_2$, 0.225 SCCM flow rate of $\text{Zr}(\text{OtBu})_4$, 0.2 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$, and 3.0 SCCM flow rate of NO_2 for film formation for 600 seconds. According to Fig. 28, by changing the duration time of the initial nuclei

5 formation, the grain size can be changed from 30 nm to 400 nm. It is difficult to grow nuclei with the distance of 30 nm or shorter. If the nuclei are formed with the distance of 400 nm or wider, amorphous film containing Pb, Ti, and Zr begins to form between the nuclei. If the
10 grain size is too small, the electric properties are deteriorated and therefore, the grain size is preferably selected corresponding to the element size.

[0078]

Though an embodiment of the present invention was
15 described above while exemplifying PZT film formation, a vapor phase growth method of the present invention is not limited to the PZT film formation methods and effective to formation of a metal oxide dielectric film whose properties can be changed by crystal orientation. The
20 metal oxide dielectric materials for a ferroelectric or high-dielectric-constant film formable to be a film by a film formation method of the present invention include oxides having general formulas; $\text{SrBi}_2\text{Ez}_2\text{O}_9$ (wherein Ez denotes Nb or Ta); $\text{EpBi}_2\text{EqO}_9$ (wherein Ep denotes Ba or Pb
25 and Eq denotes Nb or Ta); $\text{ExBi}_4\text{Ti}_4\text{O}_{15}$ (wherein Ex denotes Sr, Ba or Pb); $\text{Ey}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ (wherein Ey denotes Sr, Ba or

Pb); $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$; $(\text{Pb}_{1-y}\text{La}_y)(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$; $\text{Bi}_4\text{Ti}_3\text{O}_{12}$; SrTiO_3 , and $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$, and the metal oxide dielectric materials are not at all restricted to these materials.

[0079]

- 5 Practical examples of the foregoing ferroelectric or high-dielectric-constant metal oxide films are PTO (lead titanate: PbTiO_3), STO (strontium titanate: SrTiO_3), BTO (barium titanate: BaTiO_3), PLZT $\{(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3\}$, PNBZT $\{(\text{Pb}, \text{Nb})(\text{Zr}, \text{Ti})\text{O}_3\}$, SBT ($\text{SrBi}_2\text{TaO}_9$), $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$,
10 $(\text{Ba}, \text{Sr})\text{TiO}_3$, and the likes.

 In an example of the foregoing metal oxide film, especially a dielectric film with the perovskite type crystal structure represented by ABO_3 can be formed in two steps with different film formation conditions from
15 each other.

[0080]

 Further, in these embodiments, though the flow rate of each raw material gas was controlled by a mass flow controller, it was confirmed that a method of the present
20 invention was effective to a method in which the pressure of a film formation chamber was controlled by further using partial pressure measuring means such as a molecular weight measuring apparatus and atomic absorption spectroscopy in the case of employing a raw
25 material supply system equipped with a liquid supply type flow rate controlling apparatus and an evaporator.

[0081]

A method for fabricating a memory cell relevant to the first embodiment of the present invention is illustrated in Figs. 14. At first, an oxide film was formed on a silicon substrate by wet oxidation. After that, n-type and p-type wells were formed by ion-implantation with impurities of boron, phosphorus or the like. Then, gates and diffusion layers were formed in the following manner. At first, gate oxide films 601 were formed by wet oxidation and then polysilicon 602 was formed in film state and then etching was carried out to give gates. After a silicon oxide film was formed on the resultant polysilicon layers, etching was carried out to form side wall oxidation films 603. Next, n-type and p-type diffusion layers were formed by ion implantation with impurities of boron, arsenic or the like. Further, after a Ti film was formed on the resultant layers and reacted with silicon, the unreacted Ti was removed by etching to form Ti silicide on the gates 604 and the diffusion layers 605. Through the foregoing process, as shown in Fig. 14(A), n-type and p-type MOS type transistors isolated by the oxidized film 606 for isolated were formed on a silicon substrate.

[0082]

Next, contacts and a lower part electrode were formed as illustrated in Fig. 14(B). At first, after a

silicon oxide film or a silicon oxide film (BPSG) doped with impurities such as boron was formed as a first interlayer insulation film 607, leveling was carried out by a CMP method. Following to that, after contact holes
5 were opened by etching, the respective n-type and p-type diffusion layers were implanted with impurities and then subjected to heating at 750°C for 10 seconds. After that, Ti and TiN were formed in films as barrier metals. After tungsten layer was formed further thereon by a CVD method,
10 plugs 608 of tungsten were formed by CMP. The plugs of tungsten might be formed by etching back after CVD of tungsten. Further thereon, as a capacitor lower part electrode layer, a Ti film 609 and a TiN film 610 were successively formed by sputtering and a 100 nm thick Pt
15 film 611 was formed thereon.

[0083]

Next, a ferroelectric capacitor was formed as illustrated in Fig. 29(C). PZT of 100 nm thickness was formed by employing a method of the present invention.
20 Lead bis(dipivaloylmethanate) $\text{Pb}(\text{DPM})_2$, titanium tetra(isopropoxide) $\text{Ti}(\text{OiPr})_4$, and zirconium tetra(tert-butoxide) $\text{Zr}(\text{OtBu})_4$ were used as raw materials and NO_2 was used as an oxidizing agent. A metal oxide dielectric film of PZT 612 was obtained by film formation in
25 conditions of at 400°C of the substrate temperature and at first 0.2 SCCM flow rate of $\text{Pb}(\text{DPM})_2$, 0.05 SCCM flow

rate of $\text{Zr}(\text{OtBu})_4$, 0.25 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$, and 3.0 SCCM flow rate of NO_2 for 40 seconds and then 0.25 SCCM flow rate of $\text{Pb}(\text{DPM})_2$, 0.225 SCCM flow rate of $\text{Zr}(\text{OtBu})_4$, 0.2 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$, and 3.0 SCCM flow rate of NO_2 for 600 seconds. The total pressure of the gases in the vacuum chamber during the film growth at that time was controlled to be 5×10^{-3} Torr. The thickness of the grown film was 100 nm. Then, IrO_2 613 and Ir 614 were formed in films by a sputtering method to form a capacitor upper part electrode layer. Thereafter, the capacitor upper part electrode layer, the metal oxide dielectric film, and the capacitor lower part electrode layer were patterned to form isolated PZT capacitors by dry etching.

15 [0084]

A capacitor upper part electrode was formed thereon as illustrate in Fig. 14(D). After a silicon oxide layer was formed by a plasma CVD method as a second interlayer insulation film 615, capacitor upper part contacts and plate wire contacts were opened by etching. After WSi , TiN , AlCu , and TiN were formed in films in this order by sputtering, they were processed by etching to give a second metal wirings 616. After a silicon oxide film and a SiON film were formed thereon as passivation film 617, wiring pad parts were opened and electric properties were evaluated.

[0085]

Though, with reference to Figs. 14, description was made for the method in which isolation of capacitors were performed by dry etching after formation of the capacitor lower part electrode, the PZT film, and the IrO₂/Ir capacitor upper part electrode. However, as illustrated in Figs. 15, the method may be carried out in the following order: at first the capacitor lower part electrodes, that is, Pt/TiN/Ti, are isolated by dry etching and then the PZT film is formed, the IrO₂/Ir capacitor upper part electrode layer is formed, and after that the upper part electrodes are isolated. By this method, the film required to be dry etched is thin film. Owing to this, a finer pattern can be formed. Further, since the side faces of PZT are not exposed to plasma, introduction of defects in the PZT film can be avoided. The electric properties of the capacitors fabricated by the methods illustrated by Figs. 14 and Figs. 15 will be described below.

[0086]

5,000 of PZT capacitors with 1 μm square were connected in parallel and the properties were measured. As a result, 10 $\mu\text{C}/\text{cm}^2$ or higher value of the difference of the inversion and non-inversion electric charge was obtained to show excellent dielectric property. The fatigue property and the retention property were also

excellent. Further, by evaluation of the properties in transistors of 0.26 μm gate length, variation of threshold voltage values (V_t) of both p-type and n-type was found 10% or lower in the whole surface of a wafer and found excellent. Further, by measurement of the resistance of the capacitor lower part contacts of 0.4 μm square by a contact chain method, it was found that the resistance per single contact was 10 Ωcm or lower and excellent.

10 [0087]

Next, a method for fabricating memory cells relevant to the second embodiment of the present invention is illustrated in Fig. 16. Memory cells were fabricated in the same manner as the first embodiment up to the step forming tungsten plugs in the process. Further, Ti, TiN films were formed thereon. An AlCu film was formed by a sputtering method and first aluminum wirings 618 were formed by a dry etching method. By the above described process, the first aluminum wiring was formed on n-type and p-type MOS transistors as illustrated in Fig. 16(A).

[0088]

Then, via holes and second aluminum wirings were formed as illustrated in Fig. 16(B). At first, after a silicon oxide film or a silicon oxide film (BPSG) doped with impurities such as boron was formed as a second

interlayer insulation film 619, leveling was carried out by a CMP method. Following to that, after via holes were opened by etching, Ti and TiN were formed in films as barrier metals. After tungsten was formed in a film
5 further thereon by a CVD method, plugs 620 of tungsten were formed by CMP. The plugs of tungsten might be formed by etching back after CVD of tungsten. Further thereon, Ti and TiN were formed by a sputtering method and second aluminum wirings 621 were formed by a dry
10 etching method. Then, as a third interlayer insulation film 622, a silicon oxide film or a silicon oxide film (BPSG) doped with impurities such as boron was formed, and leveling was carried out by a CMP method. Next, via holes were opened by etching, Ti film and TiN film were
15 formed as barrier metals. After tungsten film was formed further thereon by a CVD method, plugs 623 of tungsten were formed by CMP. The plugs of tungsten might be formed by etching back after CVD of tungsten. A desired number of wiring layers might be formed by repeating
20 these aluminum wiring, interlayer film formation, and via hole formation. On the final tungsten plugs, a Ti film 624 and a TiN film 625 were successively formed by sputtering and a 100 nm thick Pt film 626 was formed thereon to give lower part capacitor electrodes.
25 [0089]

Next, a ferroelectric capacitor was formed as

illustrated in Fig. 17(C). PZT of 100 nm thickness was formed by employing a method of the present invention. Lead bis(dipivaloylmethanate) $\text{Pb}(\text{DPM})_2$, titanium tetra(isopropoxide) $\text{Ti}(\text{OiPr})_4$, and zirconium tetra(tert-butoxide) $\text{Zr}(\text{OtBu})_4$ were used as raw materials and NO_2 was used as an oxidizing agent. A metal oxide dielectric film of PZT 627 was obtained by film formation in conditions of at 400°C of the substrate temperature and at first 0.2 SCCM flow rate of $\text{Pb}(\text{DPM})_2$, 0.05 SCCM flow rate of $\text{Zr}(\text{OtBu})_4$, 0.25 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$, and 3.0 SCCM flow rate of NO_2 for 40 seconds and then 0.25 SCCM flow rate of $\text{Pb}(\text{DPM})_2$, 0.225 SCCM flow rate of $\text{Zr}(\text{OtBu})_4$, 0.2 SCCM flow rate of $\text{Ti}(\text{OiPr})_4$, and 3.0 SCCM flow rate of NO_2 for 600 seconds. The total pressure of the gases in the vacuum chamber during the film growth at that time was controlled to be 5×10^{-3} Torr. The thickness of the grown film was 100 nm. After IrO_2 film 628 and Ir film 629 were formed by a sputtering method to form a capacitor upper part electrode layer, the capacitor upper part electrode layer, the metal oxide dielectric film, and the capacitor lower part electrode layer were patterned to form isolated PZT capacitors by dry etching.

[0090]

A capacitor upper part electrode was formed thereon as illustrate in Fig. 17(D). After a silicon oxide film

was formed by a plasma CVD method as a fourth interlayer insulation film 630, capacitor upper part contacts and plate wiring contact holes were opened by etching. After each film of WSi, TiN, AlCu, and TiN was formed in this order by sputtering, they were processed by etching to give third metal wirings 631. After a silicon oxide film and a SiON film were formed thereon as a passivation film 632, wiring pad parts were opened and electric properties were evaluated.

10 [0091]

Even in the case where there is an aluminum wiring in the lower part, as same in the case as illustrated in Figs. 15, it may be allowed to carry out in the following order: at first the capacitor lower part electrodes, that is, Pt/TiN/Ti, are isolated by dry etching and then the PZT film is formed, the IrO₂/Ir capacitor upper part electrode layer is formed, and after that, the upper part electrodes are isolated. By this method, the film required to be dry etched is thin film. Owing to this, a finer pattern can be formed. Further, since the side faces of PZT are not exposed to plasma, introduction of defects into the PZT film can be avoided.

[0092]

The electric properties of the memory cells fabricated by this second fabrication method were evaluated in the same manner as used for the memory cells

fabricated by the first fabrication method.

[0093]

As a result, $10 \mu\text{C}/\text{cm}^2$ or higher value of the difference of the inversion and non-inversion electric charge was obtained to show excellent dielectric property. The fatigue property and the retention property were also excellent. Further, by evaluation of the properties in transistors of $0.26 \mu\text{m}$ gate length, variation of threshold voltage values (V_t) of both p-type and n-type was found 10% or lower in the whole surface of a wafer and found excellent. Further, by measurement of the resistance of the capacitor lower part contacts of $0.4 \mu\text{m}$ square by a contact chain, it was found that the resistance per single contact was $10 \Omega\text{cm}$ or less and excellent.

[0094]

Though in both cases of the first and the second embodiments relevant to the memory cells, description was given using tungsten for the contacts, also in the case of using polysilicon for the contacts, the ferroelectric capacitor property, the transistor property, and the contact resistance were all excellent as well. Further, in the examples, although description was given using Pt for the lower part electrodes, it was also confirmed that in the case of using Ir, IrO_2 , IrO_2/Ir , Ru, RuO_2 , TiN, or WN, the ferroelectric capacitor property, the transistor

property, and the contact resistance were all excellent as well.

[0095]

Though an example using PZT for ferroelectric capacitor formation was described, also in the case of forming BaSrTiO₃ as high-dielectric-constant capacitors using Ba(DPM)₂, Sr(DPM)₂, Ti(i-OC₃H₇)₄, and the likes, the capacitor property, the transistor property, and the contact resistance were found all excellent completely same as those of the example.

[0096]

[Effect of the Invention]

As described above, by the present invention, a ferroelectric film and a high-dielectric-constant film with controlled orientation property can be formed at a low temperature. In addition, even if a film is made thin, the characteristics of the film are scarcely deteriorated and a film with low inversion fatigue and excellent crystallinity can be obtained. By employing the present method, ferroelectric capacitors or high-dielectric-constant capacitors can be fabricated on electrodes formed on plugs such as tungsten and polysilicon without deteriorating the plugs and wiring and transistors in the lower layers to enable significant miniaturization of the capacitor surface area and to remarkably heighten the integration degree.

[Brief Description of the Drawings]

Fig. 1 is a diagrammatic illustration showing the cross-section of a vacuum chamber of an apparatus for vapor phase growth of a thin film to be employed for the present invention;

Fig. 2 is a diagrammatic illustration showing a conventional example of a reactive gas supply method in the case of using a carrier gas;

Fig. 3 shows a graph illustrating the correlation between the film thickness and the spontaneous polarization $2P_r$ in the case of PZT film growth on Pt using a sol-gel method;

Fig. 4 is a schematic diagram of a thin film formation pattern in the case of metal oxide dielectric film growth with the perovskite type crystal structure on an electrode;

Fig. 5 is a diagrammatic illustration of an apparatus for vapor phase growth of a thin film to be employed for the present invention;

Fig. 6 is a diagrammatic illustration showing the raw material supply system of an apparatus for vapor phase growth of a thin film to be employed for the present invention;

Fig. 7 is an x-ray diffraction spectrum in the case of PZT film formation in prescribed film formation

conditions alone;

Fig. 8 is an x-ray spectrum in the case of PZT film formation by optimized first film formation conditions and optimized second film formation conditions;

5 Fig. 9 shows a graph illustrating the composition ratios of Ti/Pb and Zr/Pb in the case of changing only the film formation temperature while keeping the first film formation conditions and the second film formation conditions constant;

10 Fig. 10 shows x-ray diffraction spectra in the case of keeping film formation conditions (the first film formation conditions and the second film formation conditions) constant and changing the film formation temperature;

15 Fig. 11 shows a graph illustrating the dependency of the spontaneous polarization on the film thick in the case of PZT film formation by the vapor phase growth method of the present invention;

20 Fig. 12 shows a graph illustrating the dependency of spontaneous polarization on the number of inversion times in the case of PZT film formation by a vapor phase growth method of the present invention;

25 Fig. 13 shows a graph illustrating the correlation of the initial nucleus formation time and the particle size of PZT in the first film formation conditions;

Fig. 14 is a schematic diagram showing the

5 fabrication process of memory cells, which is one embodiment of the present invention. This illustration especially shows the fabrication process in which three layers of a capacitor upper part electrode layer, a capacitor lower part electrode layer, and a metal oxide dielectric film are simultaneously separated;

10 Fig. 15 is a schematic diagram showing the fabrication process of memory cells, which is one embodiment of the present invention. These illustrations especially show the fabrication process in which a capacitor upper part electrode layer and a capacitor lower part electrode layer are separated in respective steps and a metal oxide dielectric film is left in layered state (not separated) in the memory cells;

15 Fig. 16 is a schematic diagram showing the fabrication process of memory cells, which is one embodiment of the present invention. These illustrations show the first half fabrication process of the memory cells in the case of especially a semiconductor device comprising memory cells having the aluminum-multilayered wiring structure;

25 Fig. 17 is a schematic diagram showing the fabrication process of memory cells, which is one embodiment of the present invention. These illustrations show the latter half fabrication process of the memory cells in the case of especially a semiconductor device

comprising the memory cells having the aluminum-multilayered wiring structure;

Fig. 18 shows a graph illustrating the alteration of the (Ti + Zr)/Pb composition ratio in a film in the case of altering the Pb raw material flow rate.

[Reference Numerals]

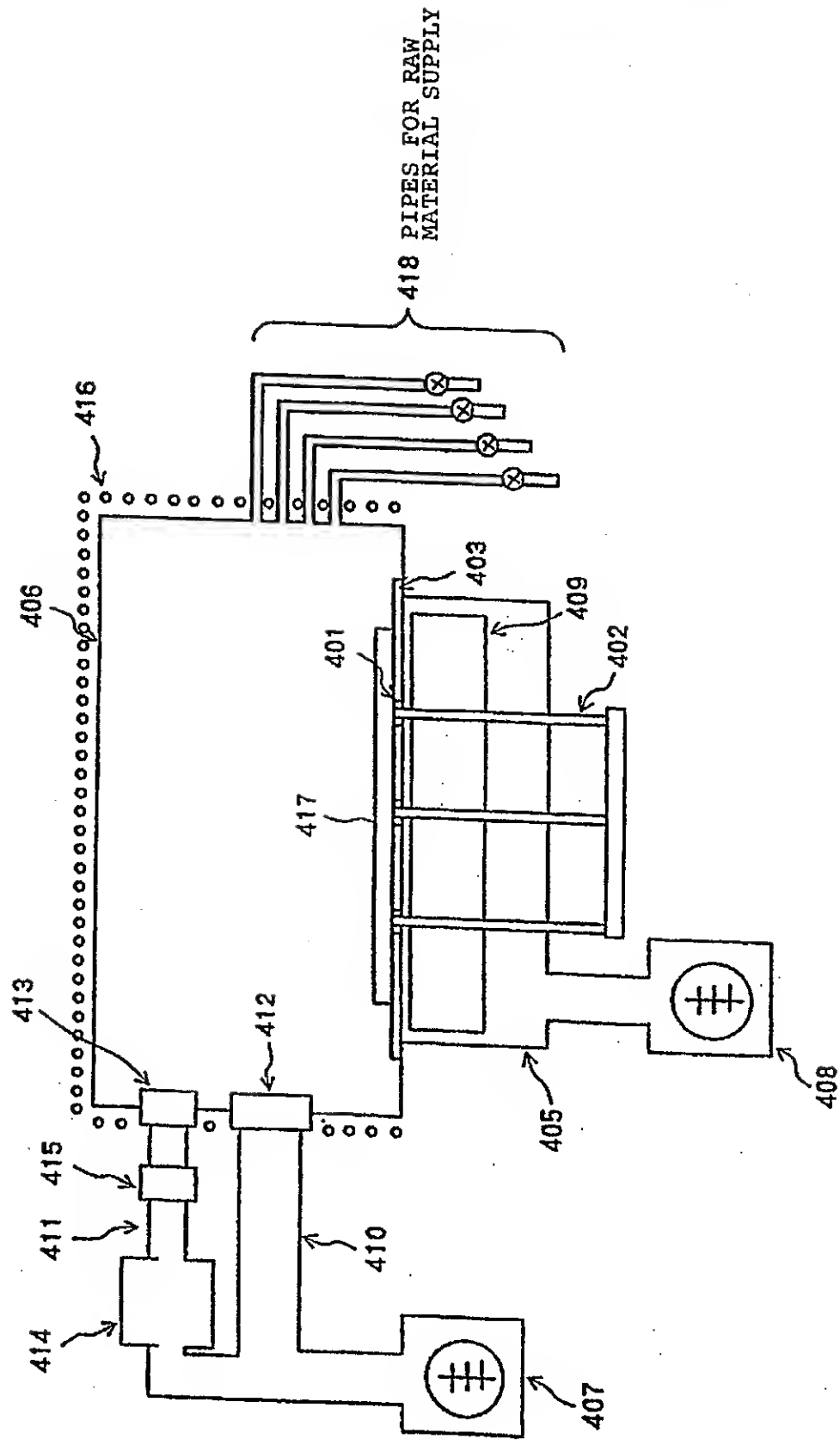
- 101 exchange chamber
- 102 vacuum chamber
- 103 raw material supply system
- 10 104 double gate valve
- 105 wafer transferring mechanism
- 106 turbo-pump
- 201 tehrmostat
- 202 bottle
- 15 203 organometal
- 204 carrier gas supply pipe
- 205 organometal material gas supply pipe
- 206 heating mechanism
- 207 growth chamber
- 20 208 wafer
- 209 gas exhaust
- 210 mass flow controller
- 401 hole
- 402 quartz pin
- 25 403 susceptor
- 405 heater chamber

406 vacuum chamber
407 turbo molecular pump
408 turbo molecular pump
409 heating mechanism
5 410 main exhaust line
411 sub exhaust line
412 main gate valve
413 valve
414 water cooling trap
10 415 conductance valve
416 heater
417 wafer
501 cylinder
502 valve
15 503 flange
504 mass flow controller
505 stop valve
506 stop valve
507 stop valve
20 508 vacuum chamber
509 water cooling trap
510 vacuum gauge
512 pump
601 gate oxide film
25 602 gate polysilicon
603 side wall oxidation film

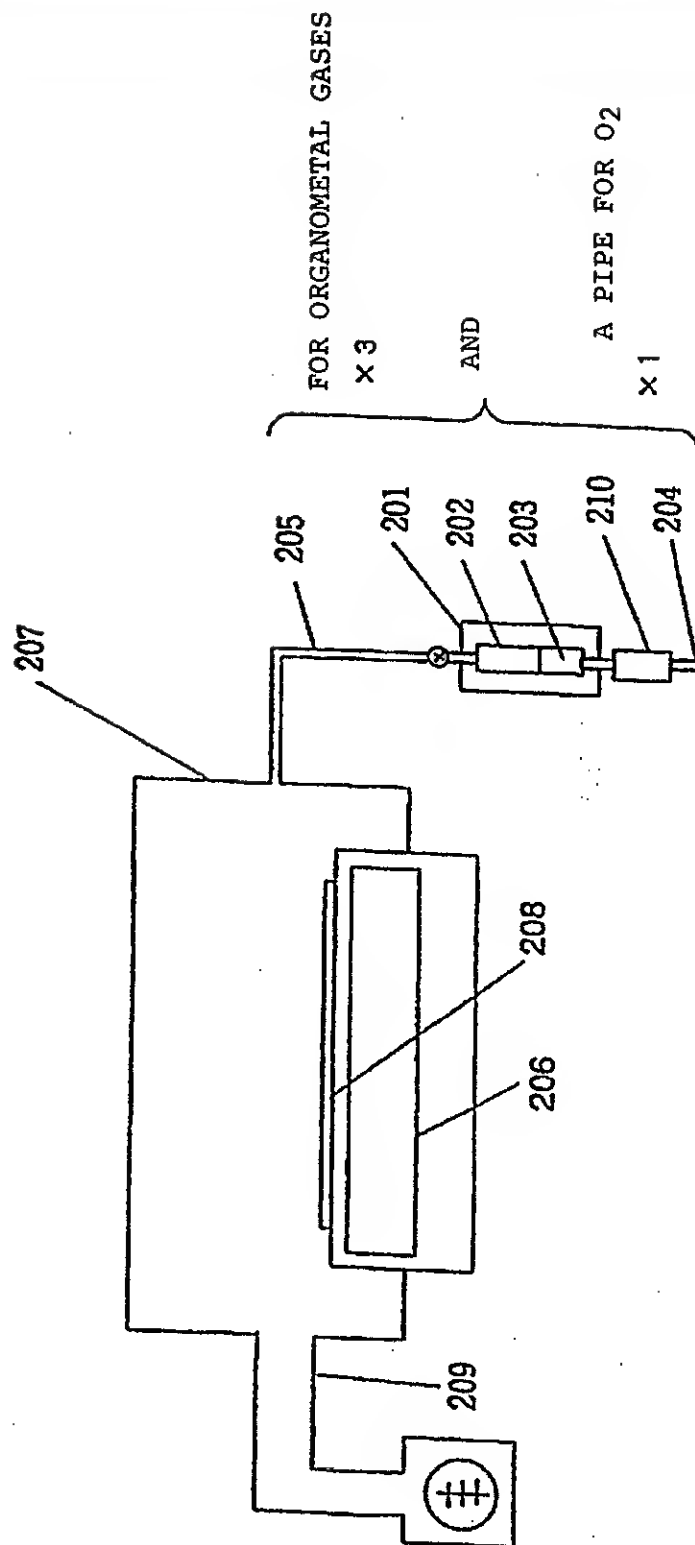
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606 oxidized film
607 first interlayer insulation film
5 608 tungsten lamp
609 Ti layer
610 TiN layer
611 Pt layer
612 PZT film
10 613 IrO₂ layer
614 Ir layer
615 second interlayer insulation film
616 second metal wiring
617 passivation film
15 618 first aluminum wiring
619 second interlayer insulation film
620 tungsten plug
621 second aluminum wiring
622 third interlayer insulation
20 623 tungsten plug
624 Ti layer
625 TiN layer
626 Pt layer
627 PZT film
25 628 IrO₂ layer
629 Ir layer

- 630 fourth interlayer insulation film
- 631 third metal wiring
- 632 passivation film
- 701 precursors of constituent elements
- 5 702 crystal nuclei

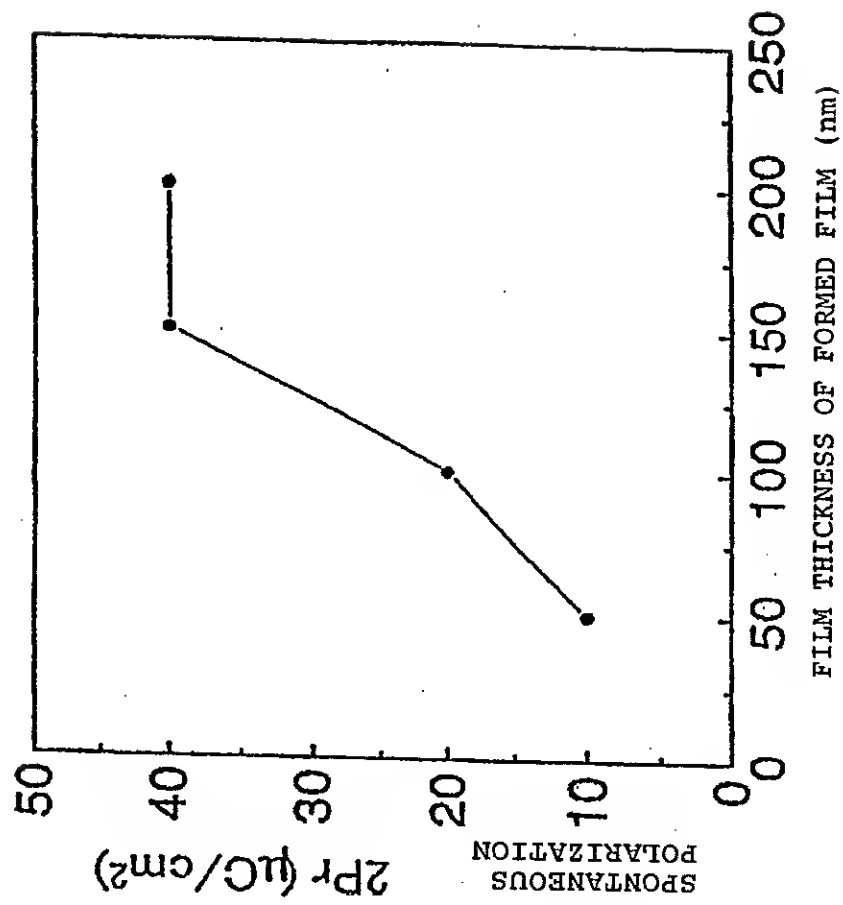
[Fig. 1]



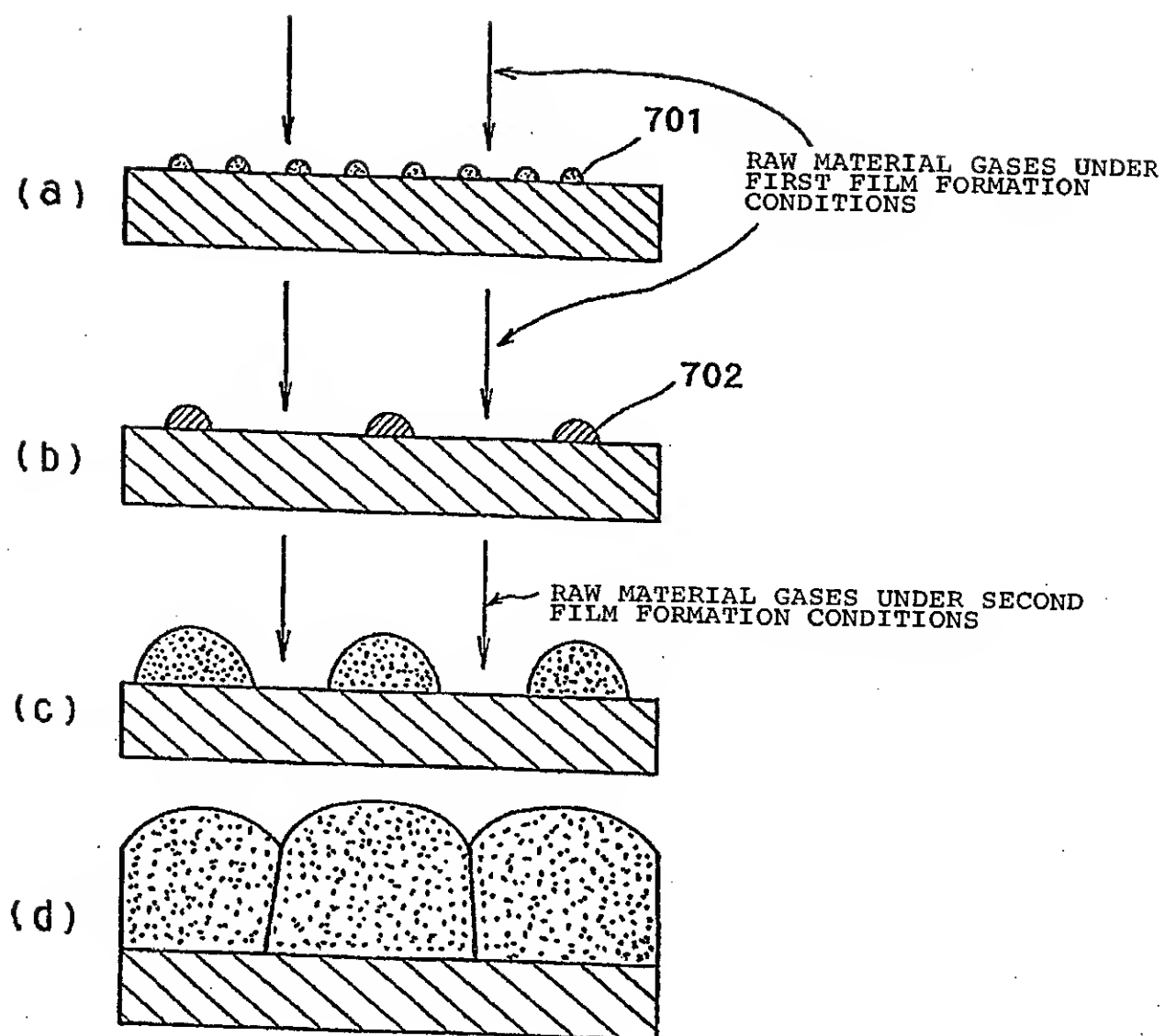
[Fig. 2]



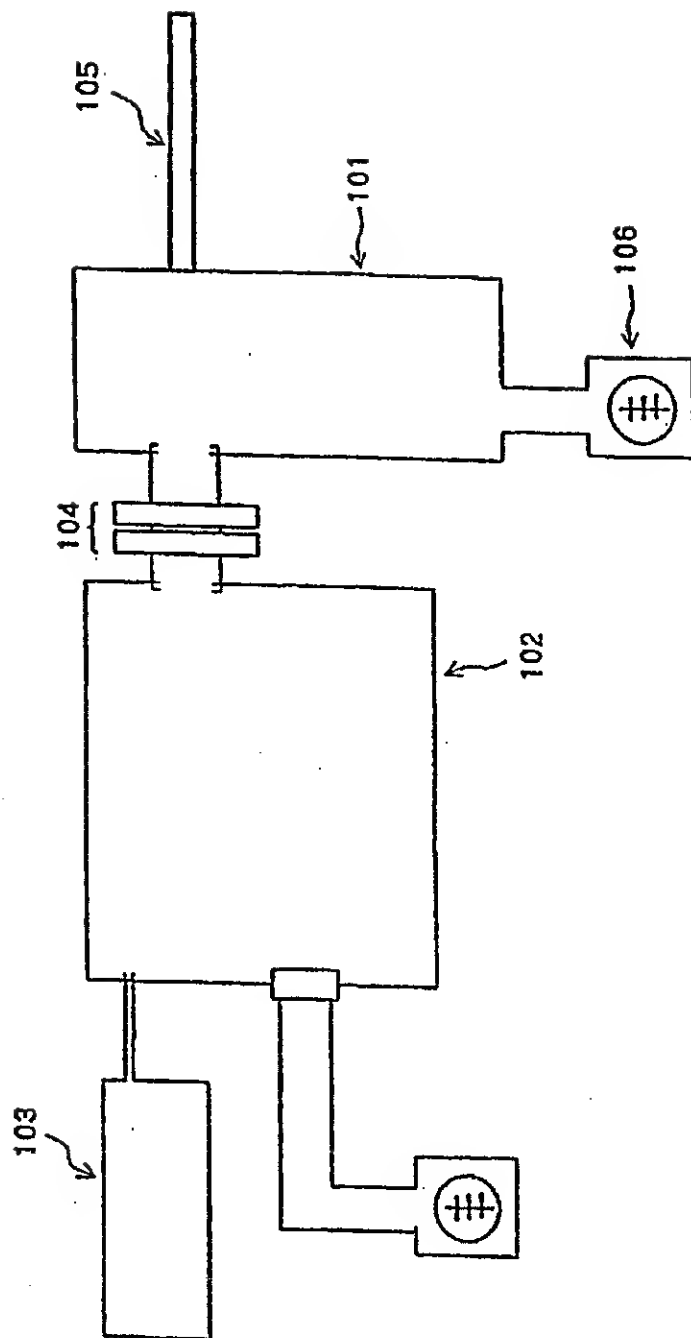
[Fig. 3]



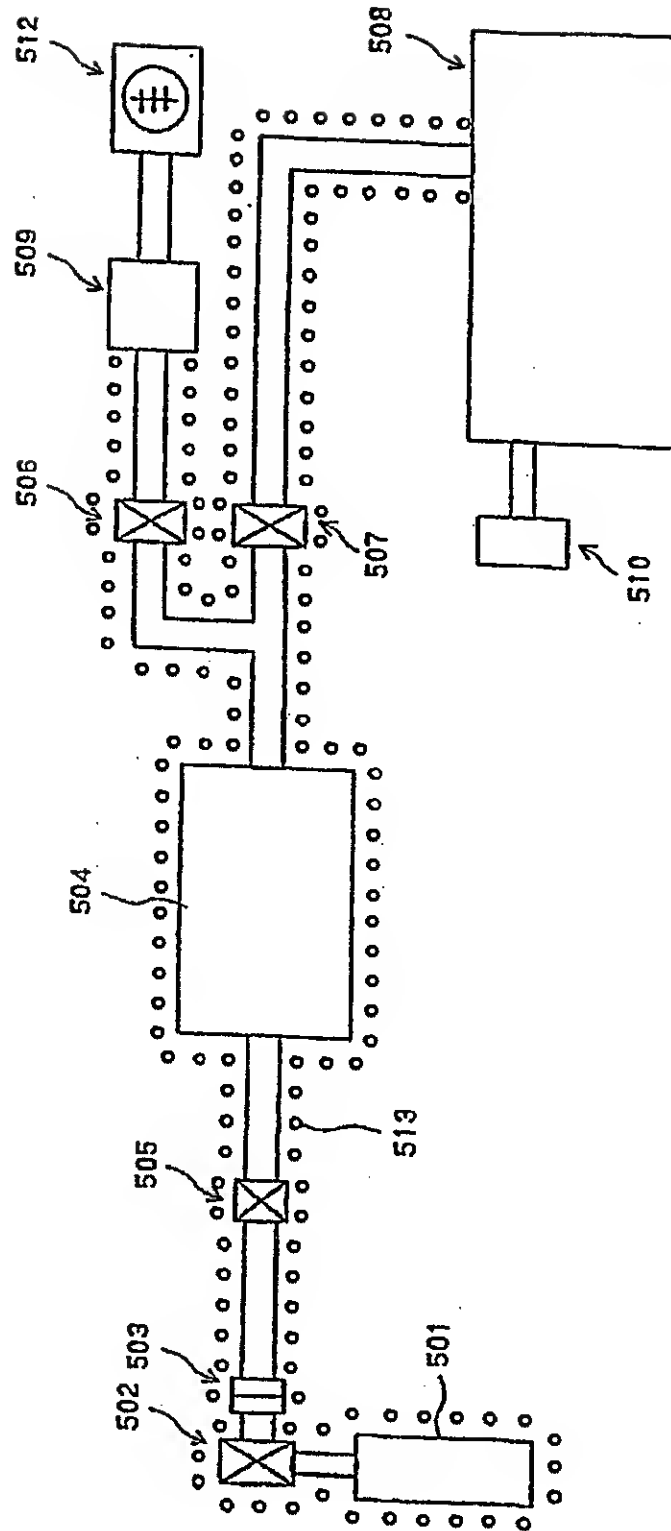
[Fig. 4]



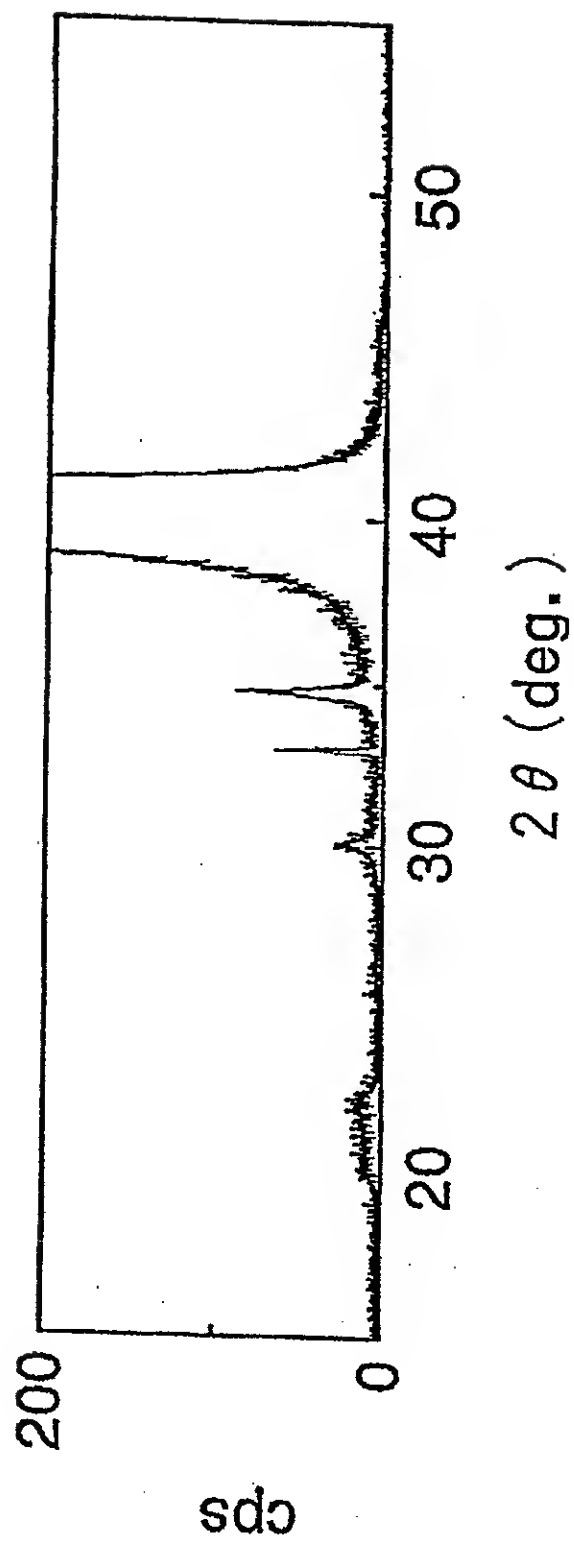
[Fig. 5]



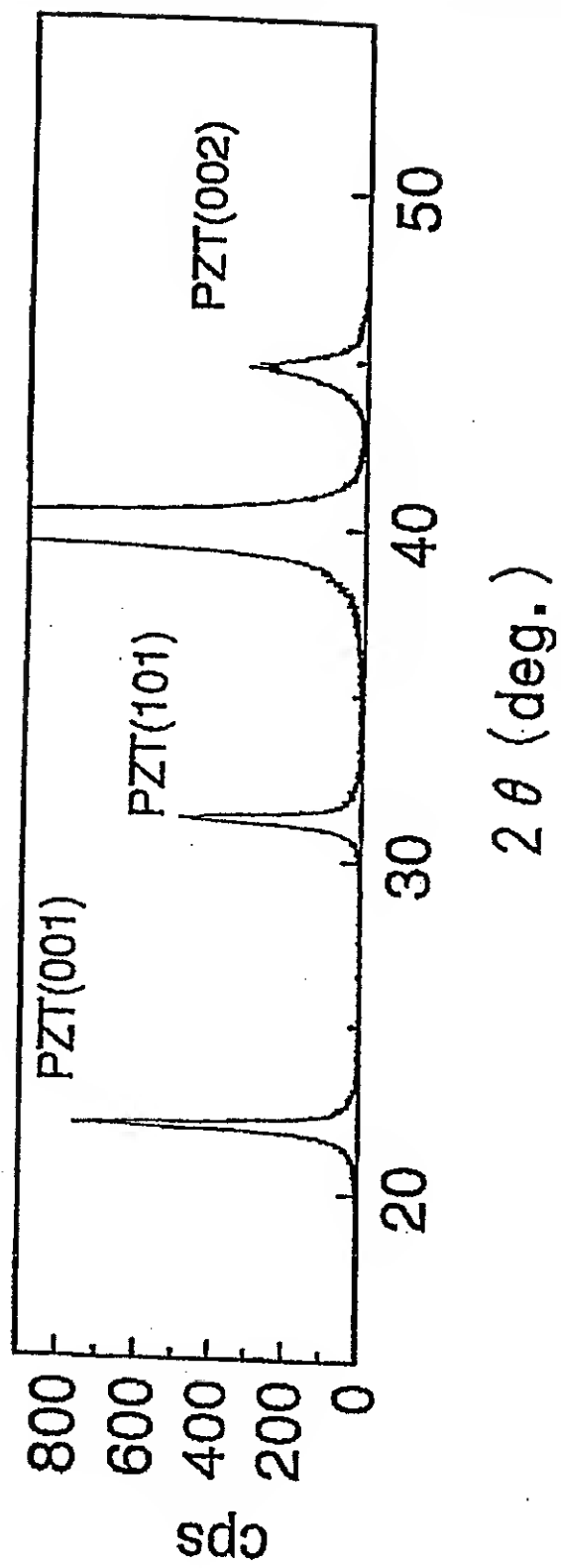
[Fig. 6]



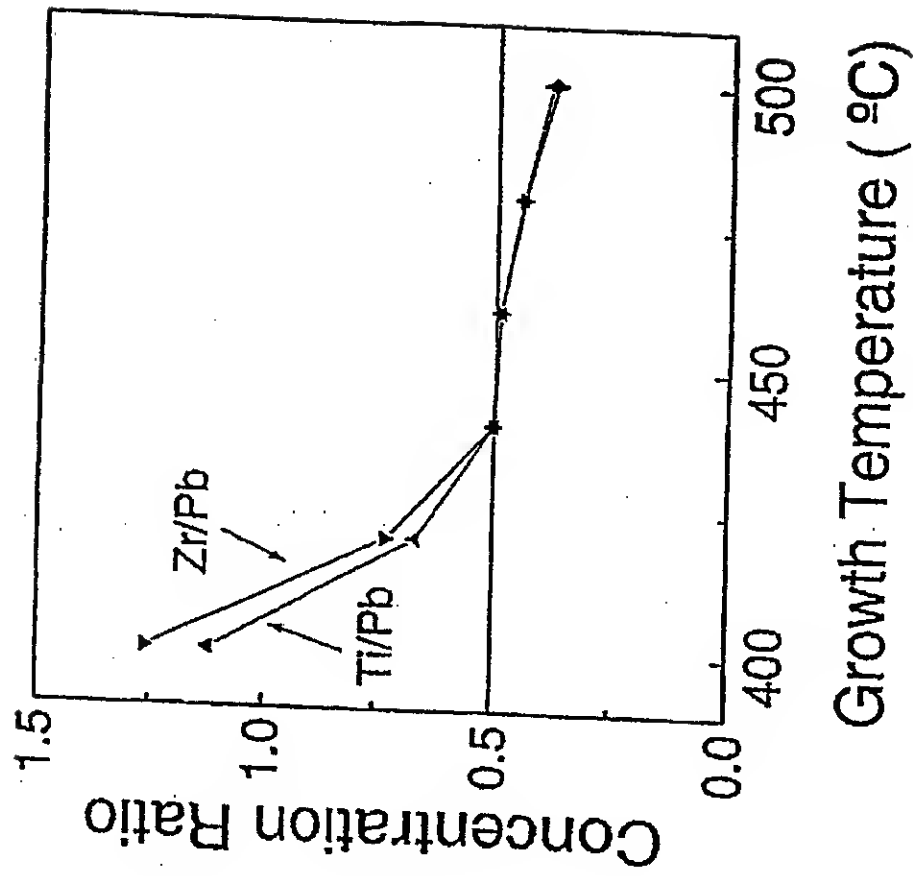
[Fig. 7]



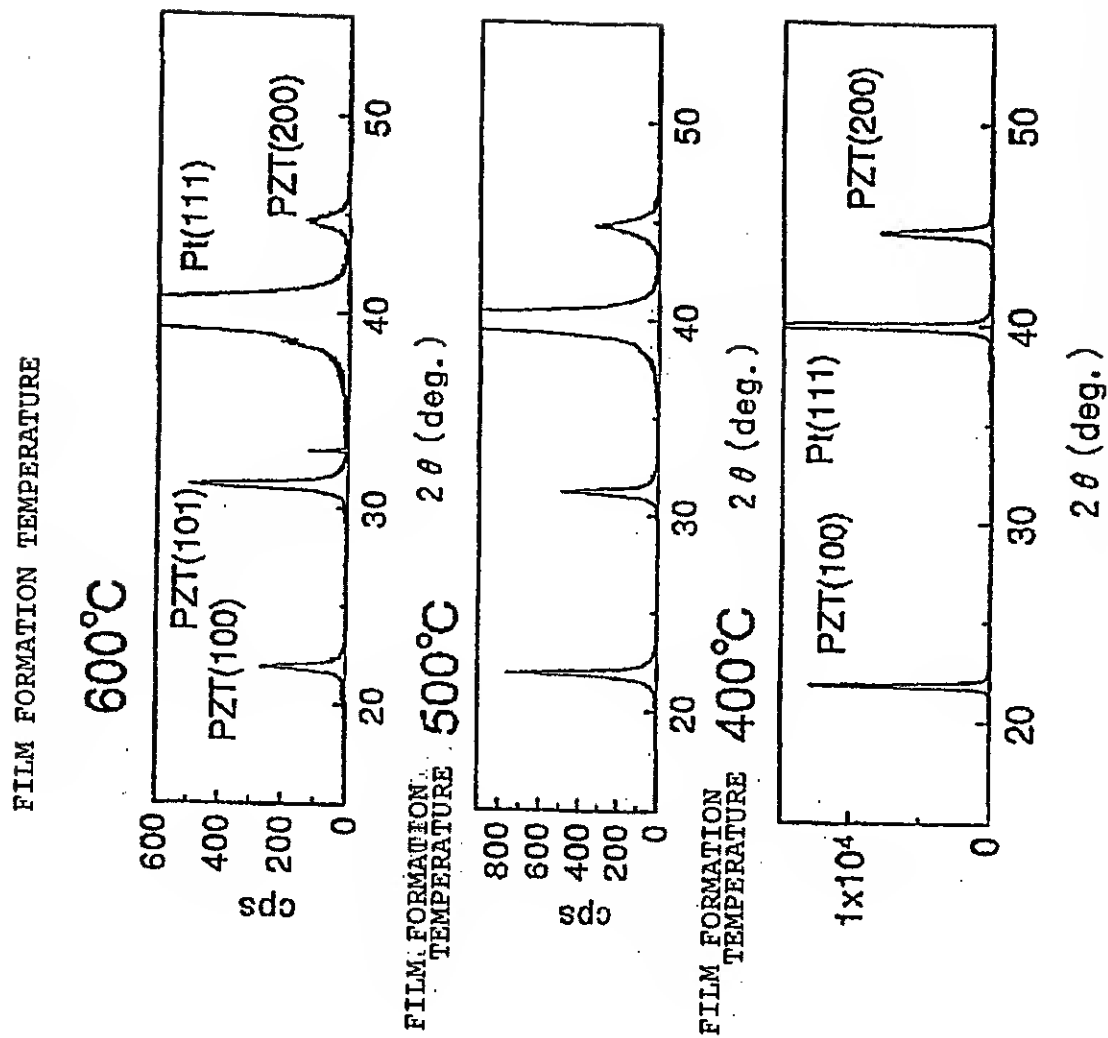
[Fig. 8]



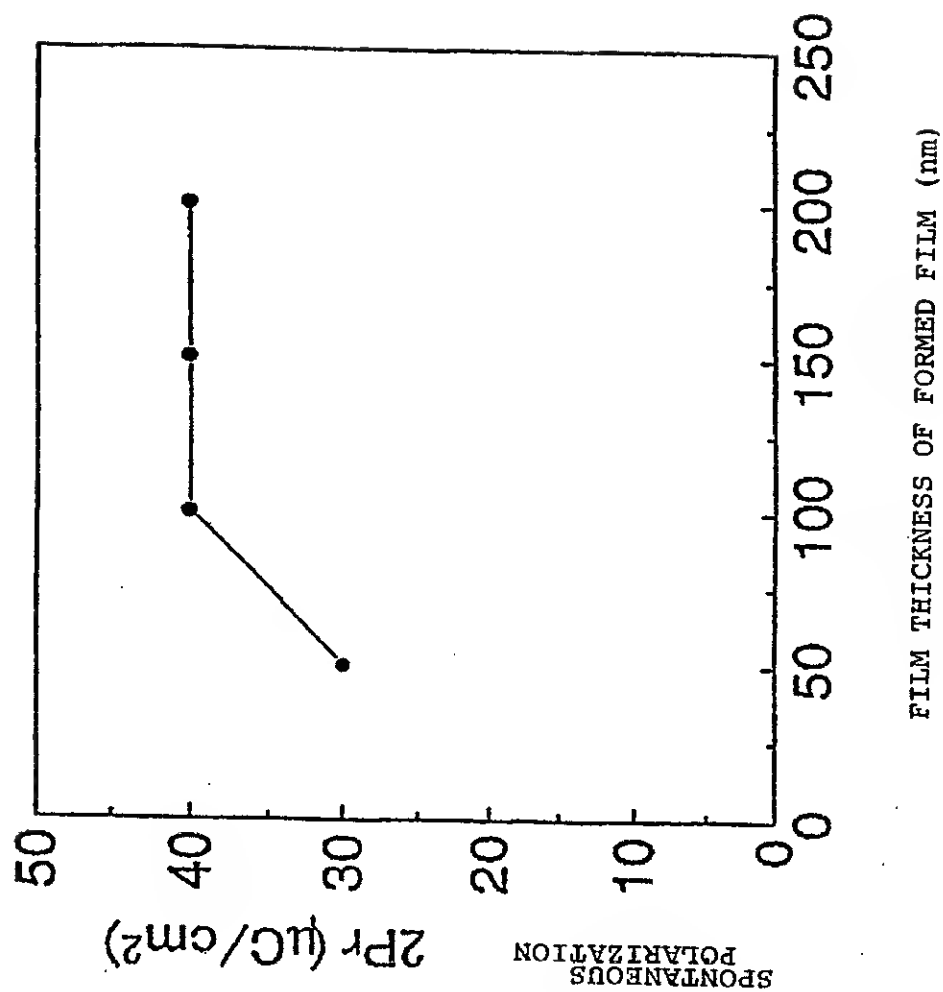
[Fig. 9]



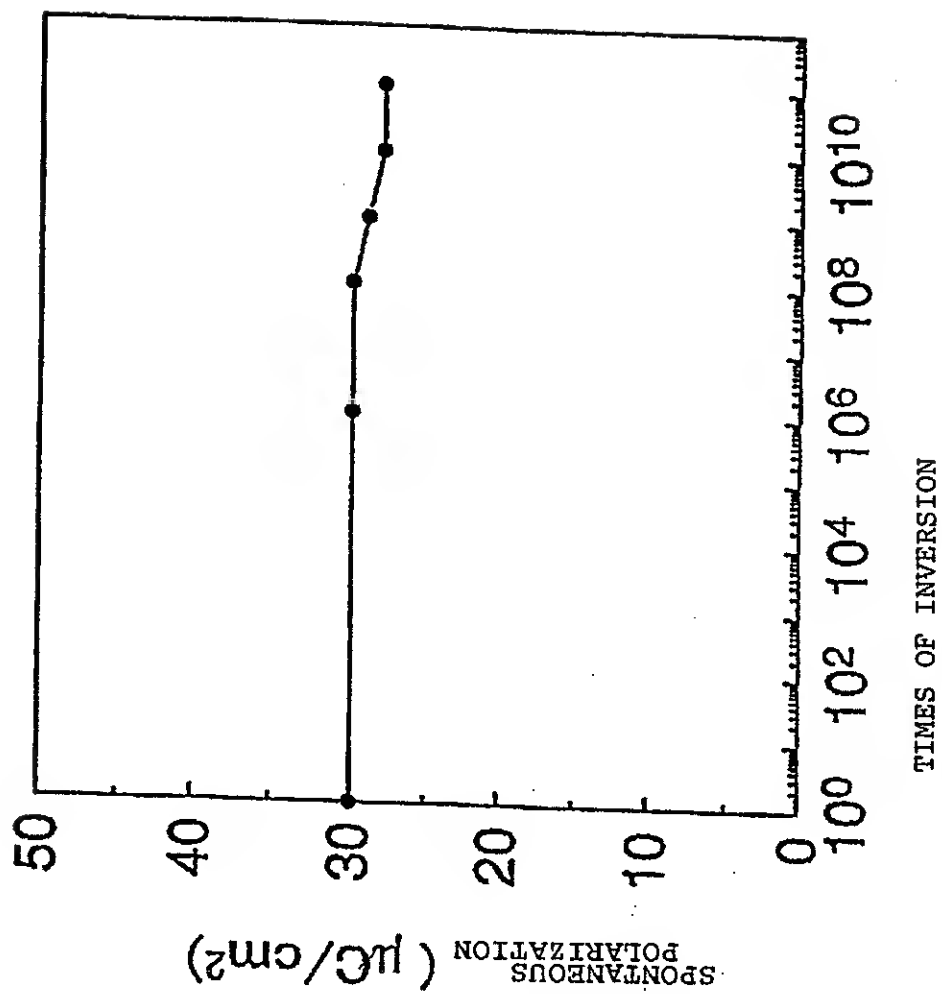
[Fig. 10]



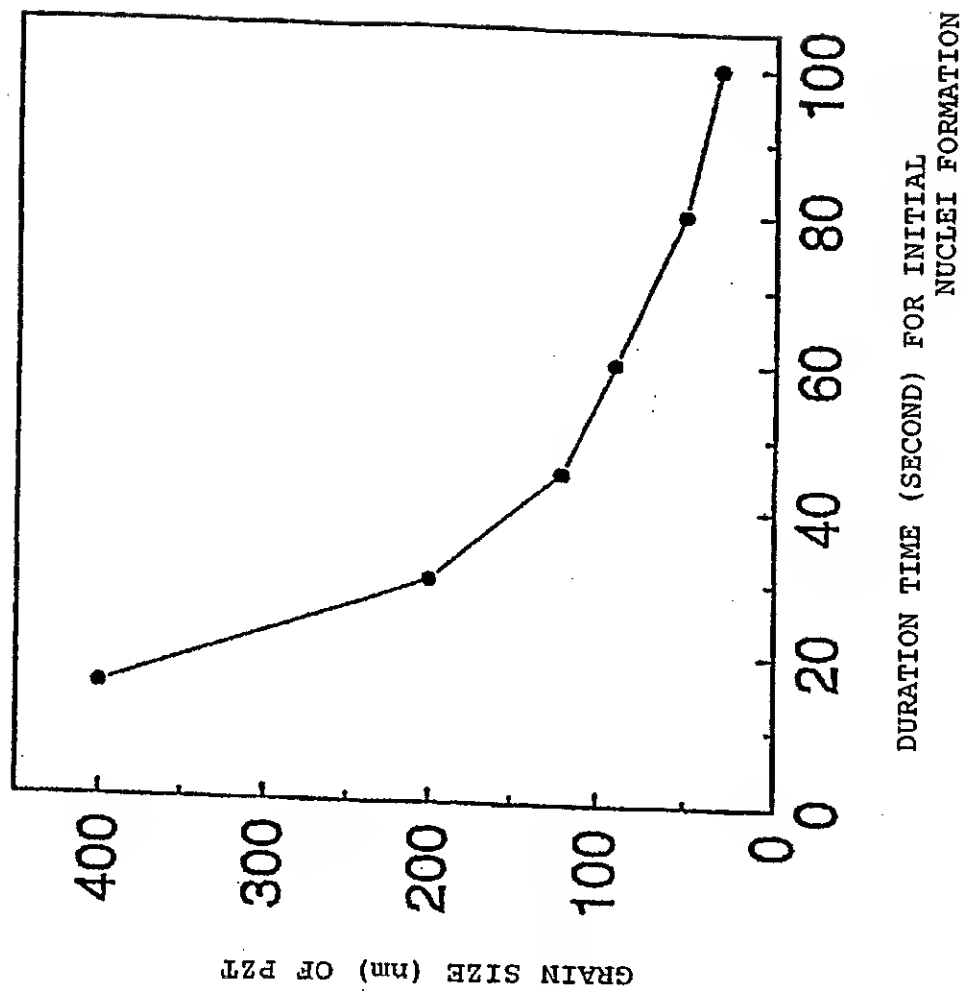
[Fig. 11]



[Fig. 12]

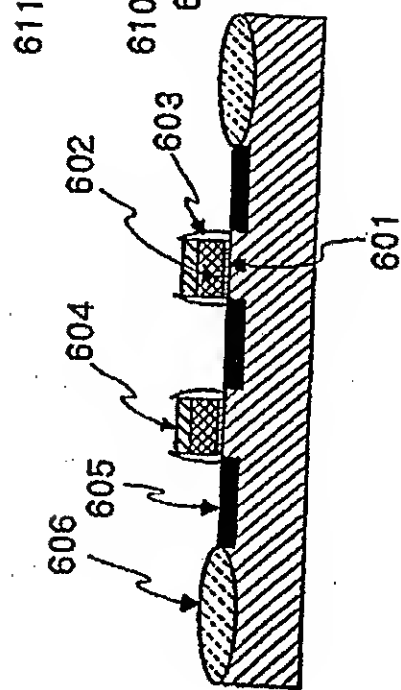


[Fig. 13]

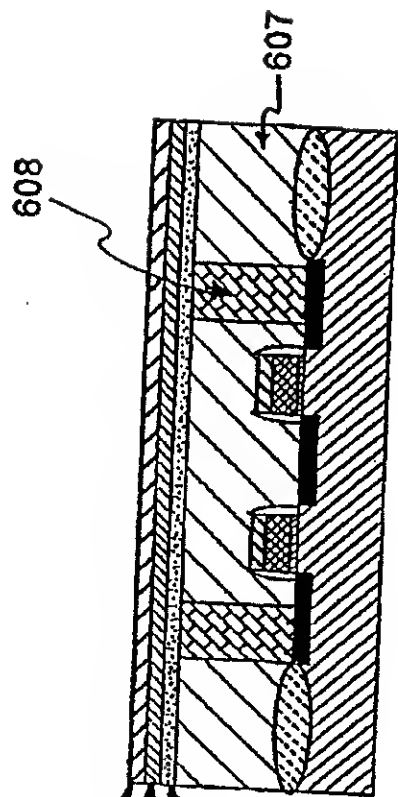


[Fig. 14]

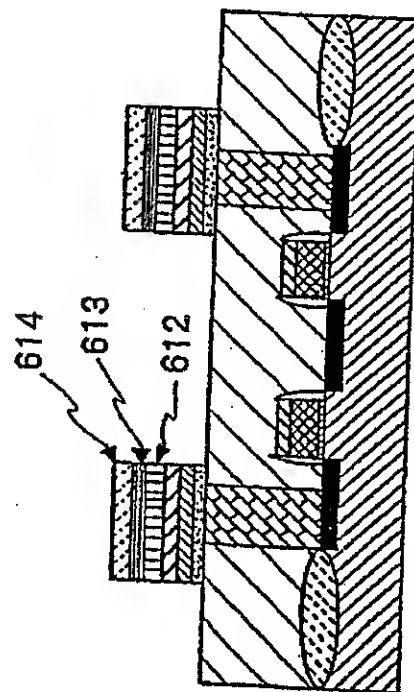
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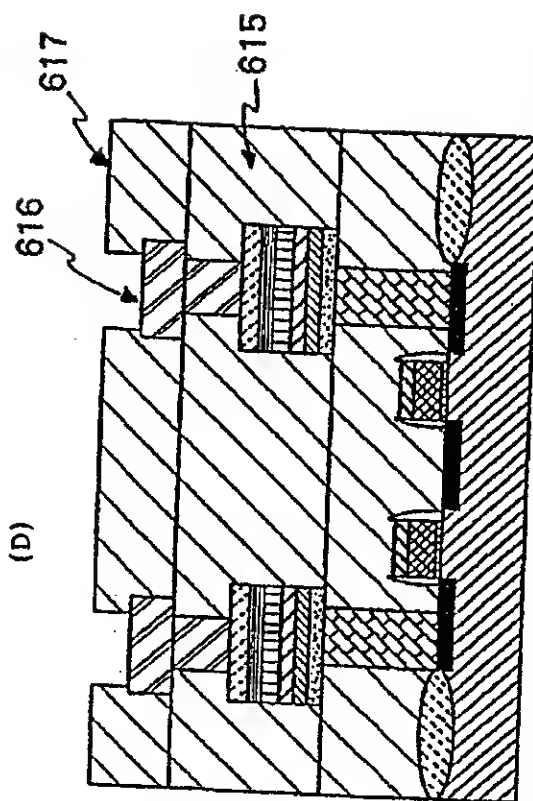
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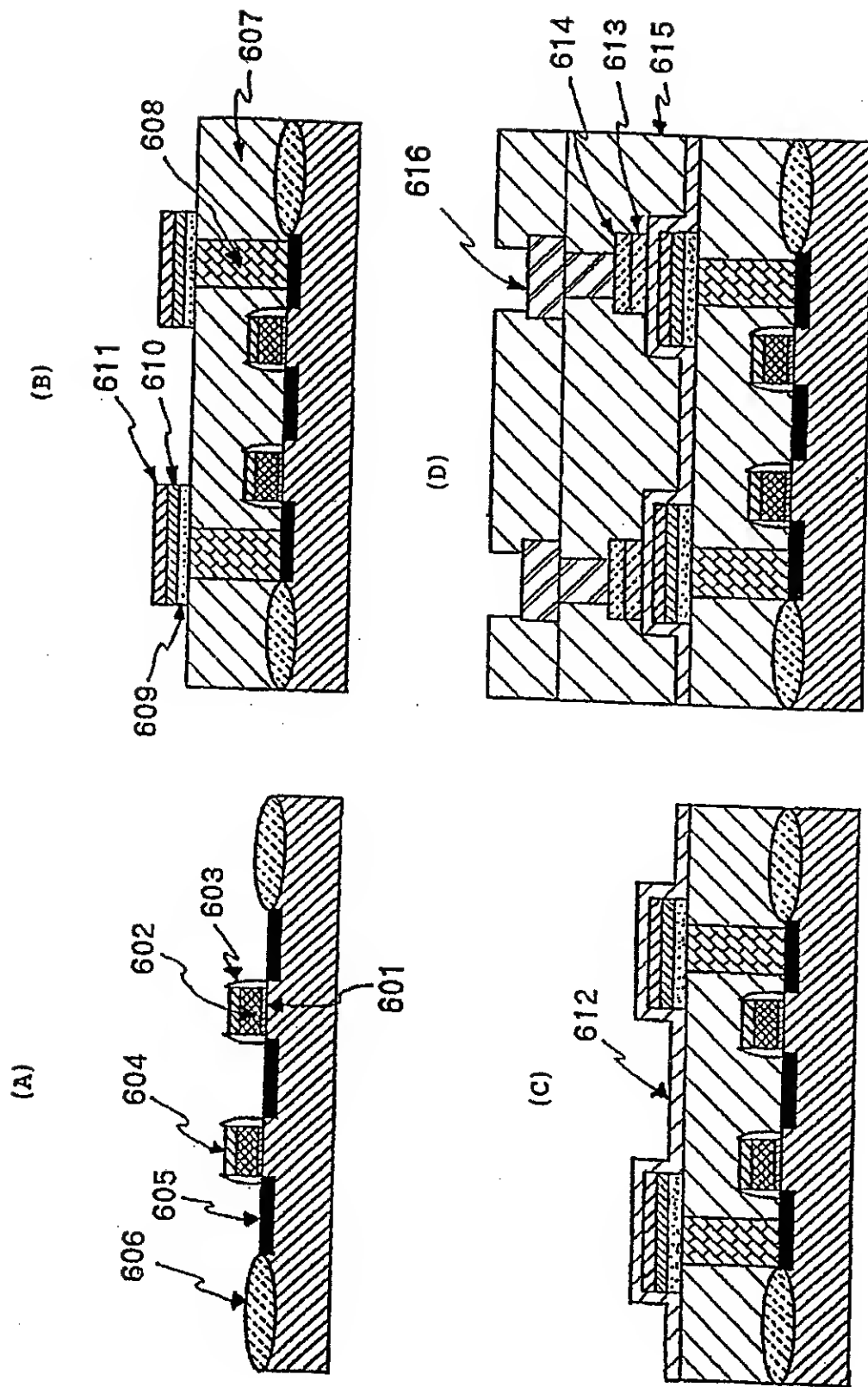
(C)



(D)



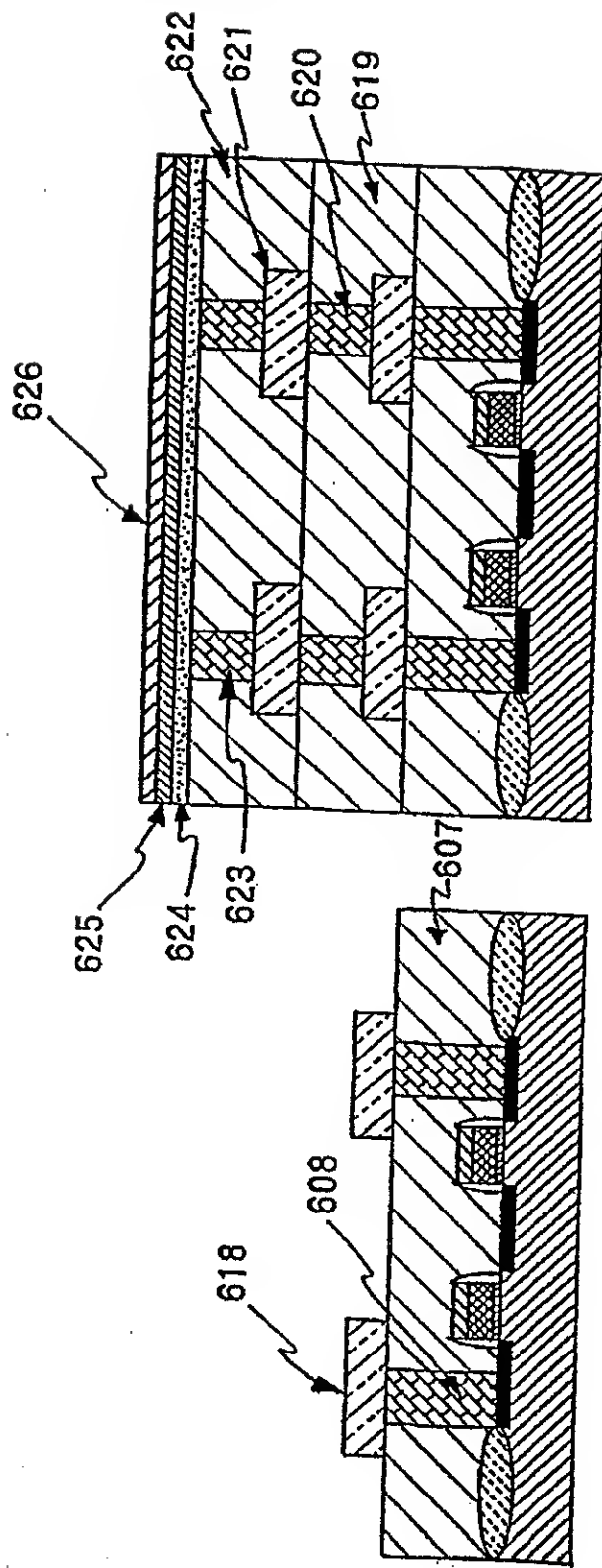
[Fig. 15]



[Fig. 16]

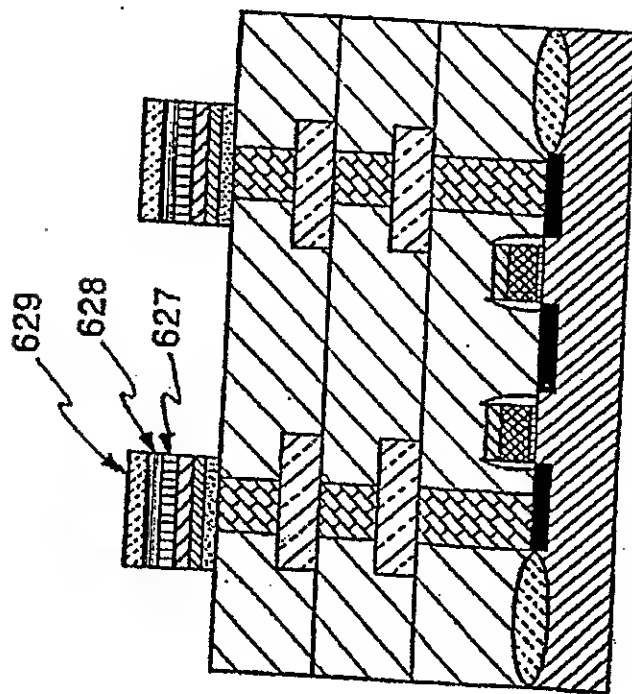
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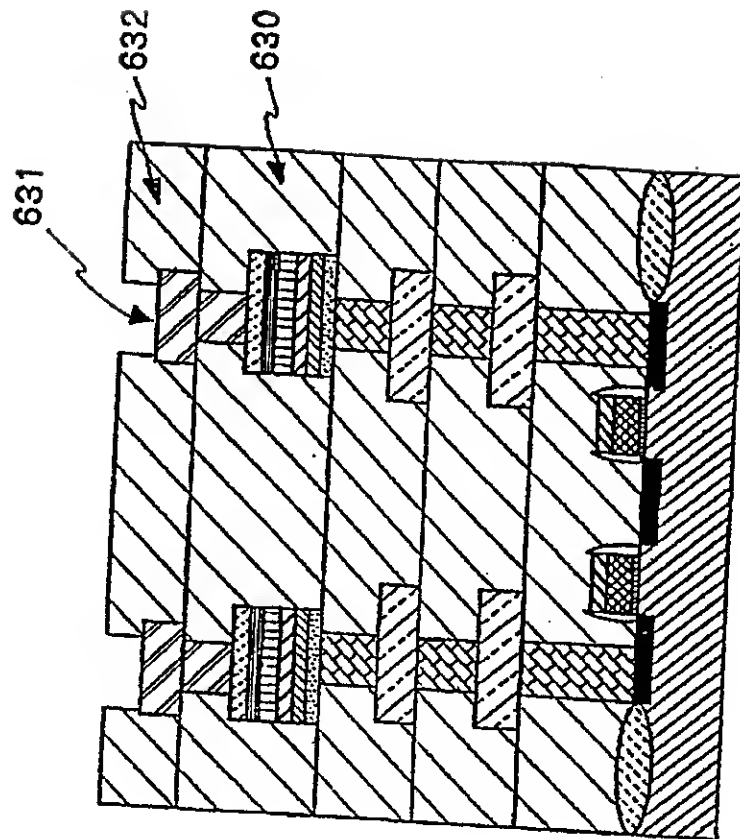


[Fig. 17]

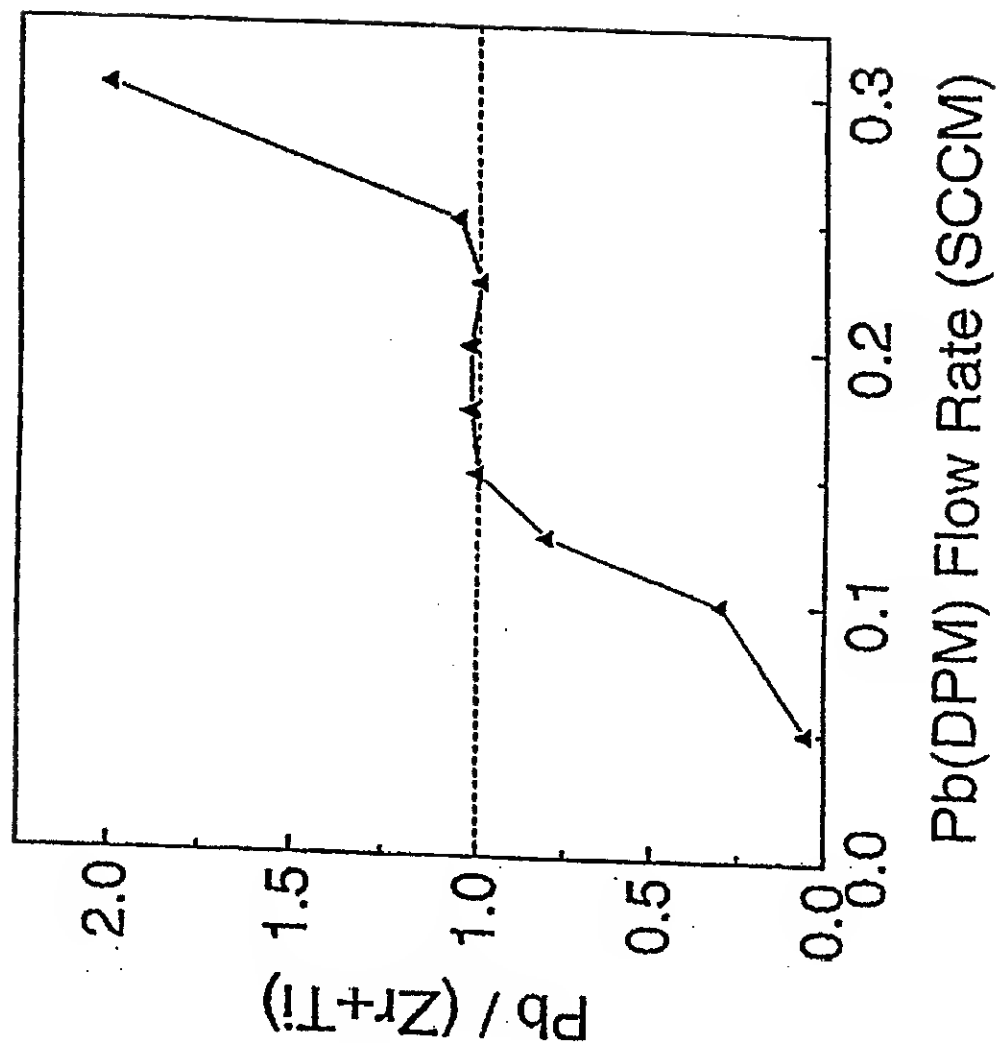
(c)



(d)



[Fig. 18]



[Document Name] Abstract

[Abstract]

[Problem]

5 The present invention provides a vapor phase growth
method of a metal oxide dielectric film and capable of
forming a metal oxide with excellent in both orientation
and crystallinity on a plug at a low temperature and
further provides a semiconductor device made to have a
fine structure, highly integrated, and multilayered and
10 metallized.

[Solution]

In contrast, according to a conventional film
formation method, film formation on a conductive material
has been carried out in same conditions through the
15 process. In the present invention, it is also possible
to select optimized conditions for the respective film
formation conditions to carry out film formation.

[Selected Drawing] Fig. 4